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INITIATION-INHIBITION RELATIONSHIPS IN STYRENE POLYMERIZATION

by

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DOCTOR OF PHILOSOPHY

Major Subject: Physical Chemistry

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Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State College
1958

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INTRODUCTION

The polymerization of styrene monomer to give high molecular weight polystyrene polymer is a subject which has received much attention and study as is witnessed by the voluminous literature on the subject which even includes an American Chemical Society Monograph[1]. This interest results not only from the industrial importance of styrene polymers and copolymers, but arises equally from the fact that the polymerization of styrene has been frequently used as a model system for the study of various aspects of polymerization in general.

In the present work, interest has centered on the free radical initiation and inhibition of styrene polymerization. Although the mechanism of these processes is fairly well understood, some of the detailed steps remain obscure. It was thought that in this respect it would be of interest to compare the stoichiometry of inhibition by several inhibitors in both thermal and initiated styrene polymerization. During the course of this work, dimethyl-N-(2-cyano-2-propyl)-ketenimine, an intermediate in the thermal decomposition of azo-*bis*-butyronitrile, was discovered and identified by Talât-Erben

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[1] R. H. Boundy and R. F. Boyer, "Styrene, Its Polymers, Copolymers and Derivatives", Reinhold Publishing Corp., New York (1952).

and Bywater[2]. This intermediate was later isolated and characterized in these laboratories by Trapp[3]. It was found[3] that dimethyl-N-(2-cyano-2-propyl)-ketenimine decomposed at a rate very close to that of azo-bis-isobutyronitrile and that in styrene it initiated polymerization. Since the study of azo-bis-isobutyronitrile as an initiator was already in progress, it was thought to be timely to investigate the stoichiometry of dimethyl-N-(2-cyano-2-propyl)-ketenimine towards one of the inhibitors already studied. In order to properly compare dimethyl-N-(2-cyano-2-propyl)-ketenimine as an initiator with azo-bis-isobutyronitrile, a collateral study was made of the efficiency of the ketenimine as an initiator in the air oxidation of cumene since azo-bis-isobutyronitrile has been studied extensively[4] in this system.

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[2] M. Talât-Erben and S. Bywater, J. Am. Chem. Soc., 77, 3710, 3712 (1955).

[3] O. D. Trapp, Unpublished Ph.D. thesis, Iowa State College Library, Ames, Iowa (1957).

[4] G. S. Hammond, J. N. Sen, and C. E. Boozer, J. Am. Chem. Soc., 77, 3244 (1955).

HISTORICAL

Styrene Polymerization

The chain character of the kinetics of polymerization in the liquid phase was recognized as early as 1932 by Staudinger[5], however, there was not general agreement as to the detailed course of polymerizations until after 1946. Much of the early work in free radical polymerizations was complicated by the fact that the effects of small amounts of molecular oxygen were not recognized. It turns out that oxygen may either inhibit[6] or initiate[7] polymerization. Induction periods, preceding normal polymerization, which resulted from the inhibitory action of oxygen gave rise to many misinterpretations and disagreements in the early literature. The early polymerization work with styrene as well as some later work has been reviewed by Boundy and Boyer[1]. More recent accounts of polymerization in general, in which styrene is treated in some detail, have been given by Flory[8] and Walling[9].

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[5] H. Staudinger, "Die hochmolekularen organischen Verbindungen", p. 151, Julius Springer, Berlin (1932).

[6] C. E. Barnes, J. Am. Chem. Soc., 67, 217 (1945).

[7] G. Goldfinger and K. E. Lauterbach, J. Polymer Sci., 3, 145, (1948).

[8] P. J. Flory, "Principles of Polymer Chemistry", Ch. 4, Cornell University Press, Ithaca, N. Y. (1953).

[9] C. Walling, "Free Radicals in Solution", Chs. 3 and 5, John Wiley and Sons, Inc., New York (1957).

The following scheme as given in Flory[10] is usually accepted as a basis to represent the mechanism of polymerization in the presence of added initiator:

(1)	$I \longrightarrow 2\,R^{\cdot}$	R_i
(2)	$R\cdot + M \longrightarrow M\cdot$	$k_a(R\cdot)(M)$
(3)	$M\cdot + M \longrightarrow M\cdot$	$k_p(M\cdot)(M)$
(4)	$2M\cdot \longrightarrow MM$ or $M' + M''$	$2k_t(M\cdot)^2$

The initiation Step 1, which gives two free radicals[11], R·, may be thermal or photochemical decomposition of an initiator. Step 2 represents addition of a primary radical from initiator to a monomer molecule to give a monomer radical which can add repeatedly to further monomer molecules in Step 3, the propagation step. The termination Step 4 is necessarily bimolecular in radicals and may give a coupling product, MM, or disproportionation products, M' and M''.

Step 2 is usually as fast or faster than the propagation Step 3, so that termination involving R· may be usually neglected. The rate constant for propagation is assumed to be independent of the number of monomer units connected to the monomer radical. If the kinetic chains are fairly long, consumption of monomer by Step 2 may be neglected in comparison with the propagation Step 3 and the rate of polymerization is given by Equations 5 - 7.

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[10] P. J. Flory, *op. cit.*, p. 110.

[11] The formation of a diradical would count as 2R·.

$$(5) \qquad R_p = -\frac{d(M)}{d\,t} = k_p(M)(M\cdot)$$

Using the steady state assumption for radical intermediates, the rate of creation of free radicals is set equal to the rate of destruction of radicals:

$$(6) \qquad R_i = 2k_t(M\cdot)^2$$

Eliminating (M•) from Equations 5 and 6, one obtains:

$$(7) \qquad R_p = k_p\ (M)\frac{(R_i)^{\frac{1}{2}}}{(2k_t)^{\frac{1}{2}}},$$

This equation holds fairly well for most homogeneous, liquid-phase polymerizations. In particular, the half order dependence on rate of initiation is quite valid[12, 13, 14, 15] for styrene. On the other hand, the dependence on monomer concentration is roughly 1.2[12, 14, 15, 16] and will be discussed later.

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[12] G. V. Schulz and E. Husemann, Z. physik. Chem., 39B, 246 (1938).

[13] J. Abere, G. Goldfinger, H. Naidus, and H. Mark, J. Phys. Chem., 49, 211 (1945).

[14] F. R. Mayo, R. A. Gregg, and M. S. Matheson, J. Am. Chem. Soc., 73, 1691 (1951).

[15] C. G. Overberger, P. Fram, and T. Alfrey, Jr., J. Polymer Sci., 6, 539 (1951).

[16] M. W. Horikx and J. J. Hermans, J. Polymer Sci., 11, 325 (1953).

Styrene is exceptional among monomers in one respect in that in the absence of added initiator it polymerizes at a measurable rate at relatively low temperatures (e.g. 8.5 per cent per hour at 120°[17]). This rate has been shown to be quite reproducible in different laboratories[18, 19]. Careful work by Goldfinger and Lauterbach[7] in which monomer was degassed several times, prepolymerized, and finally distilled into the reaction vessel, yielded a rate in good agreement with previous work. Styrene polymerization is inhibited by substances, such as quinones and nitro compounds, which are generally considered good scavengers for free radicals.

Polymerization in the absence of initiator is termed "thermal" polymerization and has also been observed for methyl methacrylate and some of its derivatives. The reproducibility of the thermal rate with styrene which has been purified by various methods is usually considered as good evidence for the rejection of initiation mechanisms involving some impurity in the monomer. Flory[20] first suggested the mechanism usually formulated to explain thermal polymeriza-

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[17] R. H. Boundy and R. F. Boyer, op. cit., p. 216.

[18] J. W. Breitenbach and W. Thury, Anz. Akad. Wiss. Wien, Math.-naturw. Klasse 83, 4 (1946); [C. A. 43, 8735 (1949)].

[19] F. R. Mayo, J. Am. Chem. Soc., 75, 6133 (1953).

[20] P. J. Flory, J. Am. Chem. Soc., 65, 2324 (1937).

tion. He postulated that n molecules of monomer could collide with enough energy to give two radicals (Equation 8) capable of adding to further monomer units thus initiating polymerization. This mechanism gives the relation for the overall rate of polymerization shown in Equation 9.

$$(8) \qquad \underline{n}\ M \xrightarrow{k_n} 2R\cdot$$

$$(9) \qquad R_p = k_p\, k_n^{\frac{1}{2}} \frac{(M)^{\frac{n}{2}+1}}{k_t^{\frac{1}{2}}}$$

Thermal polymerization has been studied most extensively with styrene and until 1953 it was generally thought that the overall rate was second order with respect to monomer concentration. Using the above thermal mechanism one can see this implies that the initiation step is bimolecular in monomer. A bimolecular initiation step fits in well with the low energy of activation (30 kcal/mole) observed for thermal initiation and it was pointed out by Flory[20] that a unimolecular initiation step could be rejected on purely energetic grounds since the energy to excite a carbon-carbon double bond to the triplet state is around 50 kcal./mole.

With bimolecular initiation, the primary product from Reaction 8 was usually considered to be the diradical I which could then grow to high molecular weight polymer by adding monomer units at both ends.

$$C_6H_5\dot{C}H\ CH_2\ CH_2\ \dot{C}HC_6H_5$$

I

In 1950 Haward[21] considered the statistical probability of formation of rings from diradicals. Calculations were based on Kuhn's[22] earlier theoretical results obtained by an application of the random flight problem to the configuration of a long polymer chain. Haward found that there should be a high probability of ring formation from a diradical. Zimm and Bragg[23] shortly thereafter, using the known chain transfer constants and termination constants for free radicals in polymer reactions and Haward's results, predicted that unless diradicals have anomalously high chain-transfer constants, diradicals should give exclusively short chain rings of 9-10 units in contrast to the very high molecular weight polymer produced in thermal polymerization. It might be added that model systems[24] (cyclic disulfides) which almost surely give diradicals photochemically do not initiate polymerization appreciably. While the cyclic azo compound, II, has been shown to initiate styrene polymerization[25], the kinetic chain-

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[21] R. N. Haward, *Trans. Faraday Soc.*, *46*, 204 (1950).

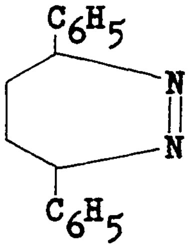
[22] W. Kuhn, *Kolloid Z.*, *68*, 2 (1934).

[23] B. H. Zimm and J. K. Bragg, *J. Polymer Sci*. *9*, 476 (1952).

[24] K. E. Russell and A. V. Tobolsky, *J. Am. Chem. Soc.*, *76*, 395 (1954).

[25] S. G. Cohen, S. Hsiao, E. Saklad, and C. H. Wang, *J. Am. Chem. Soc.*, *79*, 4400 (1957).

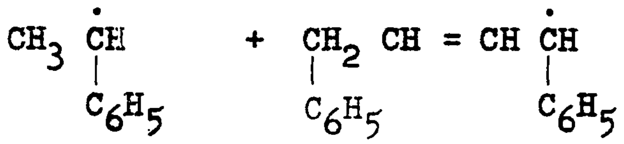
length, which is defined as the rate of polymerization divided by the rate of initiation, is low (8-10 monomer units) if the rate of initiation is taken to be equal to the rate of decomposition of the azo compound. Formation of low polymer would fit in with the above conclusions about diradicals being able to give only low molecular weight polymer although the study of II does not exclude the possibility that the rate of production of diradicals may be much lower than the rate of decomposition due to a competing, non-radical decomposition yielding simply two molecules of styrene and one of nitrogen.



II

In 1953 Mayo[19] extended the study of the overall order of the thermal polymerization from the range of 2-8 M, which had been previously studied, to concentrations as low as 0.02 M. He found that at concentrations below 2 M he got a better fit to a five-halves order in monomer concentration than to second order. At higher concentration it was impossible to say which order the data fit best. Mayo concluded that the order of the initiation step was termolecular and suggested that one might obtain the two radicals, III and IV.

The energetics of hydrogen transfer seem feasible and the measured entropy of activation for thermal polymerization is low.



$$\mathrm{CH_3}\underset{\mathrm{C_6H_5}}{\overset{\bullet}{\mathrm{CH}}} \quad + \quad \underset{\mathrm{C_6H_5}}{\mathrm{CH_2}}\ \mathrm{CH = CH}\ \underset{\mathrm{C_6H_5}}{\overset{\bullet}{\mathrm{CH}}}$$

III IV

Inhibitor Action in Polymerization

Just as it was observed that certain substances such as peroxides, when added to a monomer in small amounts, would initiate polymerization, it was observed certain other substances, such as quinones, nitric oxide, nitro compounds, when added in very small amounts to an initiated system, would inhibit polymerization. As a class these substances are termed polymerization inhibitors. It might be well to note at this point that antioxidants, which comprise another class of inhibitors, are sometimes used to stabilize monomers. Antioxidants prevent the formation of peroxides in monomer exposed to air and by preventing the formation of initiator, prevent the formation of polymer from monomer. Antioxidants do not inhibit thermal or initiated polymerization in the absence of oxygen. It should also be noted that while some substances are both antioxidants and polymerization inhibitors many are not.

Some polymerization inhibitors such as nitrobenzene only slow the rate of polymerization, while others, such as quinones, virtually completely stop all polymerization until they are used up at which time the rate of polymerization may rise again to the uninhibited rate[26]. The time during which little or no polymerization takes place is termed the induction period. In the case of a reactive inhibitor such as quinone, the sharp increase in rate of polymerization after the induction period permits one to determine the length of the induction period with great precision. Foord[26], who in 1940 made the first systematic study of polymer inhibition, termed a substance an inhibitor if it gave a well defined induction period, and a retarder, if the inhibition was weaker and the induction period consequently less well defined. More precise investigations later made it possible to establish that the difference between an inhibitor and a retarder was only quantitative rather than qualitative[27, 28]. Compounds such as nitrobenzene which at one time[26] were called retarders are now simply termed weak inhibitors.

According to the kinetic scheme of polymerization (Equations 1 - 4), in order to inhibit the overall rate of poly-

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[26] S. G. Foord, J. Chem. Soc., 48 (1940).

[27] P. D. Bartlett, G. S. Hammond, and H. Kwart, Discussions Faraday Soc., 2, 342 (1947).

[28] G. V. Schulz, Chem. Ber., 80, 232 (1947).

merization, one must essentially alter the chain mechanism such that the contribution of the chain propagation Step 3 is nil. One dramatic way of doing this is to employ a stable free radical which is unable to initiate polymerization but which is very reactive towards other free radicals. Ordinarily in polymerizations, the termination step which is bimolecular in radical concentration is not very competitive with the propagation step. Although the termination rate constant is much larger (being essentially diffusion controlled) than that of the propagation reaction, the concentration of radicals in polymerizing systems is so low (e.g., 10^{-8} M in a solution of styrene initiated by benzoyl peroxide at 90°) that the propagation step, which is only first order in radical concentration, dominates. Although the rate constant for termination between a growing chain radical and a stable free radical may be somewhat smaller than that for the reaction between two growing chain radicals, stable radicals may have dramatic effects on polymerization rates since they may be maintained at relatively high concentration levels (e.g., 10^{-2} M). It has indeed been found[29] that stable free radicals such as diphenylpicrylhydrazyl decrease the polymerization rate during an induction period more than any other known inhibitors.

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[29] P. D. Bartlett and H. Kwart, J. Am. Chem. Soc., 72, 1051 (1950).

Another method, which also ultimately changes the nature of the termination step, is to introduce another substrate besides monomer which competes with monomer for growing chains, but which yields a stabilized free radical which is unable to add further to monomer units. "Dead" radicals derived from inhibitors are consumed either with bimolecular reactions with each other or with growing polymer chains. This could take place in three ways: by direct addition to an inhibitor molecule, X, in analogy with the propagation step:

(10) $$M\cdot + X \longrightarrow X\cdot$$

or, by an atom abstraction reaction:

(11) $$M\cdot + HX \longrightarrow MH + X\cdot$$

or, finally, by disproportionation:

(12) $$M\cdot + X \longrightarrow M' = CH_2 + \cdot XH$$

It is easy to see that if X· is somewhat reactive yet it may react again with monomer as well as proceeding through a termination step. Such behavior would lead to copolymerization, if addition occurs (Equation 10), or to a process termed "chain transfer" if the additive reacts by Equation 11 or Equation 12.

There is one further general aspect of inhibition that should be pointed out. One might expect that with some inhibitors, Reactions 10, 11, and 12 would consume the inhibitors stoichiometrically in the termination step. Since one may, by using the steady state approximation for transient intermediates, set the rate of creation of radicals equal to the rate of termination of radicals, it is possible that the rate of consumption of inhibitor could be a measure of the rate of initiation. Admittedly, there are serious complications which can arise. For example, two processes of different stoichiometry might go on simultaneously or the products formed from the inhibitor in stopping two chains might still be able to stop further chains[30]. However, since the rate of initiation can give interesting information about the mechanism of decomposition of the initiator, a large number of workers have attempted to use inhibitors to study initiation rates with varying success. Foord[26], in his work in 1940 with chloranil, applied this method to determine a value for the activation energy for thermal polymerization of styrene. The result is in reasonable agreement with the value determined by Mayo[19] which is presently accepted as the best available.

Quinones form an interesting group of inhibitors which have been studied in enough detail to allow one to see how

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[30] Usually isolation and identification of end products of termination reactions is very difficult and sometimes the results of such studies are not unequivocal.

some of them, at least, fit into the above scheme. Early work established two things which one would almost surely expect. First, during the induction period extremely low molecular weight polymer is formed and as the induction period ends the molecular weight of the polymer formed climbs to the value characteristic of uninhibited polymerization under the same conditions of solvent and temperature[31]. Two reduced residues are incorporated in the polymer and the polymer formed during the inhibition period contains more quinone-termination product than does the polymer formed as the inhibition period is ended. These facts certainly fit with the above mechanistic scheme.

The chemistry of quinone-inhibition of polymerization is complicated. Inhibition is usually[32, 33] considered to proceed either by disproportionation to give unsaturated polymer plus a hydroquinone radical or by addition of the polymer radical either at oxygen or at a ring-carbon atom to give a relatively stable radical which is sometimes termed a "sigma" complex. Price[34] and Price and Read[35] favor attack on the

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[31] G. Goldfinger, I. Skeist, and H. Mark, *J. Phys. Chem.* *47*, 578 (1943).

[32] P. J. Flory, "Principles of Polymer Chemistry", p. 164, Cornell University Press, Ithaca, N. Y. (1953).

[33] C. Walling, "Free Radicals in Solution", p. 166, John Wiley and Sons, Inc., New York (1957).

[34] C. C. Price, "Reactions at Carbon-Carbon Double Bonds", p. 86, Interscience Publishers, Inc., New York (1946).

[35] C. C. Price and D. H. Read, *J. Polymer Sci.*, *1*, 44 (1946).

ring whereas Cohen[36] favors attack at the oxygen. Bartlett, Hammond, and Kwart[27], working with the polymerization of allyl acetate initiated by benzoyl peroxide, established that chloranil was incorporated in the polymer and that at least 27 per cent of the residues contained ether linkages which implies that some attack on the oxygen of the quinone occurs. These workers also obtained spectrophotometric evidence for both oxygen and ring addition products. In the case of thermally initiated styrene, Breitenbach and Renner[37] find that chloranil is attacked at oxygen and that a 1:1 copolymer is formed at 100°.

Rembaum and Szwarc[38], from evidence obtained in their study of competitive addition rates of methyl radicals to a variety of unsaturated compounds, infer that the above reactions go through a "sigma" complex with addition to the ring being the only reaction. They suggest other products result from rearrangement during isolation. This seems unlikely and while one should bear this work in mind, the result is based entirely on kinetic data. Furthermore, one should note that methyl radicals are unlike allyl (or styryl) radicals. An

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[36] S. G. Cohen, J. Am. Chem. Soc., 67, 17 (1945); 69, 1057 (1947).

[37] J. W. Breitenbach and A. J. Renner, Can. J. Research, 28B, 509 (1950).

[38] A. Rembaum and M. Szwarc, J. Am. Chem. Soc., 77, 4468 (1955).

interesting possibility for the course of inhibition reaction with quinones is suggested by the work of Hammond, Boozer, Hamilton and Sen[39] on the mechanism of inhibition in the air oxidation of hydrocarbons. They advance evidence that the primary inhibition step involves formation of a loose "pi" complex rather than hydrogen abstraction. A similar mechanism gives quite a reasonable explanation for the experimental results observed in the inhibited polymerizations. Earlier work with the chain transfer of styrene in bromobenzene[40] as well as more recent work in photochlorination[41] and an electron spin-resonance study[42] of air oxidation all give evidence which especially suggests a common mechanism involving "pi" complexes.

Cohen[36] found the stoichiometry of benzoquinone inhibition of benzoyl peroxide-initiated styrene polymerization was approximately one quinone to two growing chains. More recent work by Bevington, Ghanem, and Melville[43] using both ^{14}C-

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[39] G. S. Hammond, C. E. Boozer, C. E. Hamilton, and J. N. Sen, J. Am. Chem. Soc., 77, 3238 (1955).

[40] F. R. Mayo, J. Am. Chem. Soc., 75, 6133 (1953).

[41] G. A. Russell, J. Am. Chem. Soc., 79, 2977 (1957).

[42] O. L. Harle and J. R. Thomas, J. Am. Chem. Soc., 79, 2974 (1957).

[43] J. C. Bevington, N. A. Ghanem, and H. W. Melville, J. Chem. Soc., 2822 (1955).

labeled benzoquinone and labeled azo-bis-isobutyronitrile indicated that between 0.53 and 1.85 quinone molecules are incorporated in each polymer chain. These authors[43] interpreted this to mean one quinone molecule stopped two chains (termination by coupling) and that a small amount of copolymerization occurred simultaneously.

Mayo and Gregg[44] noted an interesting result with benzoquinone in the thermal polymerization of styrene. He measured the rate of consumption of inhibitor and found that at 100° a minimum of 17 times as much quinone disappeared as could be accounted for on the basis of the thermal initiation rate calculated from the molecular weight and amount of polymer formed. Mayo and Gregg suggested that copolymerization was taking place. Bartlett, Hammond and Kwart[27] had previously noticed the same effect and suggested that perhaps benzoquinone counted roughly 1:1 at 60° because the copolymerization reaction took place only at the higher temperature. Russell and Tobolsky[45] found, however, the same effect at 60°. There workers also compared the rate of disappearance of diphenylpicrylhydrazyl under conditions of the thermal polymerization with the rate of initiation calculated from the rate of polymerization and a

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[44] F. R. Mayo and R. A. Gregg, J. Am. Chem. Soc., 70, 1284 (1948).

[45] K. E. Russell and A. V. Tobolsky, J. Am. Chem. Soc., 75, 5052 (1953).

relation between rate of initiation and rate of polymerization in initiated systems. The discrepancy was even greater in this case. The disappearance of the hydrazyl was zero order in hydrazyl and second order in monomer concentration. This is in agreement with similar data of Chapiro, Durup, and Grosmangin[46]. Russell and Tobolsky suggested that the hydrazyl and quinone might be counting diradicals as well as a monoradical process which gives high polymer. If the number of diradicals exceeded by a large amount the monoradicals, the difference between the rate of thermal initiation and the rate of consumption of inhibitor, as well as the second order dependence on monomer concentration of the rate consumption of inhibitor, would be explained. Mayo[40] in his work on thermal polymerization not only measured the kinetic order with respect to monomer of the rate of formation of high molecular weight polymer, but made a careful isolation of "low" molecular weight fractions which consisted mostly of dimers. Mayo noted that if the amount of low molecular weight polymer formed were ascribed to diradicals, his results would confirm the work of Russell and Tobolsky.

It should be noted that while diphenylpicrylhydrazyl in some cases apparently gives 1:1 stoichiometry in stopping radicals[29], its reaction is not simply coupling at the nitro-

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[46] A. Chapiro, J. Durup, and J. Grosmangin, *J. chim. phys.*, *50*, 482 (1953).

gen atom. Nuclear substitution by the reactive radical sometimes occurs, followed by tautomerization of a hydrogen atom, giving a hydrazine as a final product. This appears to be the case with methyl methacrylate[47] where the hydrazyl is incorporated into the polymer molecule as a hydrazine which cannot be removed by precipitation of the polymer, but which can be re-oxidized by lead dioxide to a compound having a spectrum similar to that of picrylhydrazyl. Further, the hydrazyl has been shown[48] to give false stoichiometry in counting radicals produced from the decomposition of azo-*bis*-isobutyronitrile in inert solvents. Also, Hammond *et al.*[48] found, as had other workers[45, 46], that small traces of oxygen gave additional complications. While the hydrazyl is one of the most potent radical inhibitors known, results from its use must be interpreted with caution.

By using a moderately elaborate kinetic analysis, which includes both copolymerization and inhibition, and by measuring rates of polymerization during inhibition, Kice[49] has been able to evaluate rate constants for both processes for a large number of inhibitors in methyl methacrylate and methyl acrylate.

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[47] A. Henglein, *Makromol. Chem.*, *15*, 188 (1955).

[48] G. S. Hammond, J. N. Sen, and C. E. Boozer, *J. Am. Chem. Soc.*, *77*, 3244 (1955).

[49] J. L. Kice, *J. Am. Chem. Soc.*, *76*, 6274 (1954); *J. Polymer Sci.*, *19*, 123 (1956).

He found that the tendency for benzoquinone, 2,6- and 2,5-dichloroquinone to copolymerize with monomer is rather small and that copolymerization of chloranil is nearly twice as important as any of the other three inhibitors in methylacrylate. Copolymerization of methyl methacrylate with chloranil was 200 times as important as was copolymerization with any of the other quinones. This agrees with Breitenbach's[37] observation of a 1:1 copolymerization of chloranil with styrene at 100°.

One type of inhibition which has not received much serious attention until recently is inhibition by radicals derived from solvent by chain transfer. Chain transfer is normally[50] considered as an atom abstraction process in which a growing polymer chain, M·, interacts with any other molecule in solution, SH, to give a new radical, S·, and a "dead" polymer MH. (A halogen, such as bromine, may also be abstracted and conceivably the atom abstraction could be from M· to leave an unsaturated, "dead" polymer.)

$$M\cdot + SH \xrightarrow{k_f} S\cdot + MH \qquad (13)$$

Atom abstraction is followed addition of S· to monomer to start another polymer chain:

$$S\cdot + M \xrightarrow{k_s} M\cdot \qquad (14)$$

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[50] P. J. Flory, op. cit., p. 136.

Reaction 14 is usually considered to be very fast in comparison to the normal propagation step of polymerization. If this is valid, the rate of polymerization will be unaltered although the molecular weight will be lowered in proportion to the number of times this process takes place during the normal life of a kinetic chain. As a first approximation, only chain transfer to solvent need be considered in the polymerization of styrene initiated by azo-bis-isobutyronitrile. A solvent such as benzene has only small effect on molecular weight, a solvent such as carbon tetrachloride has a large effect, and a mercaptan has an extreme effect.

Burnett and Loan[51] have considered the effect on the rate of polymerization of chain termination by solvent-derived radicals. The effect is necessarily one of inhibition since chain termination process is accelerated. By considering the usual kinetic scheme for polymerization, together with Equations 13 and 14, they derive Equation 17 for the rate of polymerization assuming the following termination Steps 4, 15, and 16:

$$\begin{array}{lll} (4) & M\cdot + M\cdot \xrightarrow{k_{tmm}} & \\ (15) & M\cdot + S\cdot \xrightarrow{k_{tms}} & \text{Inactive products} \\ (16) & S\cdot + S\cdot \xrightarrow{k_{tss}} & \end{array}$$

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[51] G. M. Burnett and L. D. Loan, Trans. Faraday Soc., 51, 216, 219 (1955).

$$(17)\quad R_p = \frac{k_p\, R_i^{\frac{1}{2}}\, (M)^2}{(k_{tmm}\, (M)^2 + 2\, k_{tsm}\, \frac{k_f}{k_s}\, (M)(SH) + k_{tss}\, \frac{k_f^2}{k_s^{\,2}}\, (SH)^2)^{\frac{1}{2}}}$$

Burnett and Loan[51] suggest that this may be the reason the kinetic order in monomer concentration is 1.2 rather than 1.0 in the polymerization of styrene. They noted orders other than one in the literature for several monomers and examined the rates of polymerization of methyl methacrylate, methyl acrylate, and vinyl acetate as a function of concentration in benzene solutions. They measured initial rates dilatometrically and varied the solvent concentration over wider limits than had been done before. For methyl methacrylate they found a first order dependence down to 20 per cent monomer. At lower concentrations the order increased greatly. For methyl acrylate they observed a high order in monomer concentration at high concentrations. The order dropped to around one at intermediate monomer concentrations and again increased at low monomer concentrations. For vinyl acetate, the rate decreased very rapidly upon adding small amounts of benzene and went assymtotically to zero with decreasing monomer concentration. By assuming reasonable rate constants in Equation 17 for the temperature of their work and by varying the ratio $\frac{k_f}{k_s}$, they were able to successfully reproduce the form of their experimental curves.

Bartlett and Hiatt[52] have recently done an interesting investigation of the thermal initiation by styrene in which they used ethyl thioglycolate as a solvent. Ethyl thioglycolate is an excellent chain transfer agent for styrene. If large numbers of diradicals, which could not for the most part initiate long chains, were produced in the thermal polymerization of styrene, one might expect a good chain transfer agent to increase the rate of initiation of long kinetic chains many-fold. This did not happen. They also tested Equation 17 for their reaction and did not get a correct fit to their experimental points for variations in monomer concentration. At equimolar concentrations of monomer and mercaptan they were able to obtain a rate dependence or time which implied that the initiation step is termolecular with respect to monomer concentration. Their proposed mechanism was like Mayo's and involved hydrogen transfer to give two separate radicals.

Finally, Schulz[53] and Schulz and Kammerer[54] have proposed a scheme for a logical classification of inhibitors:

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[52] P. D. Bartlett and R. Hiatt. Unpublished research done at Harvard University, Cambridge, Massachusetts and presented in a Special Chemistry Seminar on May 1, 1958 by Dr. R. Hiatt at the Chemistry Department, Iowa State College, Ames, Iowa.

[53] G. V. Schulz, Ber., 80, 232 (1947); Makromol. Chem., 1, 94 (1947).

[54] G. V. Schulz and H. Kammerer, Ber. 80, 327 (1947).

I. Inhibitors which accelerate chain termination.

p-nitroaniline only

II. Inhibitors which quench the initiation step.

none

III. Inhibitors which do both I and II.

e.g. 1,8-dinitronaphthalene, hydrazobenzene, tetraphenyloctatetraene

IV. Inhibitors which initiate polymerization but which also accelerate chain termination to a greater extent.

e.g. nitrostyrene, quinones

He studied a wide variety of inhibitors using thermally-initiated styrene polymerization at 100° and arrived at the assignment of one of the above classes by simultaneously measuring the rate and degree of polymerization as a function of time and comparing them to the uninhibited rate and uninhibited degree of polymerization.

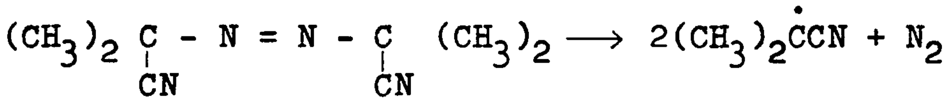
This work is often ignored perhaps because the workers were not always careful to exclude oxygen.

Nature of the Initiation Process

Initiators of free-radical polymerization include a large number of compounds which undergo homolytic dissociation at temperatures between 70 and 200°. Typical are peroxides, such as benzoyl peroxide and di-*tert*-butyl peroxide, and azo compounds, such as azo-*bis*-isobutyronitrile (ABN). The following are simplified mechanisms for the decomposition of the three compounds mentioned. Details of ABN decomposition will be discussed later in more detail.

(1) $(CH_3)_3\ COO\ C(CH_3)_3 \rightarrow 2(CH_3)_3\ CO\cdot \longrightarrow CH_3\cdot + CH_3COCH_3$

(2) $(C_6H_5CO_2)_2 \longrightarrow 2C_6H_5CO_2\cdot + C_6H_5\cdot + CO_2$

(3)


$$(CH_3)_2\underset{\displaystyle CN}{\underset{|}{C}} - N = N - \underset{\displaystyle CN}{\underset{|}{C}}\ (CH_3)_2 \longrightarrow 2(CH_3)_2\dot{C}CN + N_2$$

Two complications must be considered when one chooses an initiator for use in model experiments. The first is chain transfer reactions which may occur with some initiators. Tobolsky and coworkers[55] have determined the extent of such reactions for several initiators. They find that benzoyl peroxide and ABN are free of this complication in styrene and methyl methacrylate. Di-*tert*-butyl peroxide chain transfers quite appreciably with growing methyl methacrylate radicals. The second complication is that an initiator may undergo induced decomposition in the presence of free radicals. This

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[55] B. Baysal and A. V. Tobolsky, *J. Polymer Sci.*, *8*, 529 (1952); D. H. Johnson and A. V. Tobolsky, *J. Am. Chem. Soc.*, *74*, 938 (1952).

is the case with benzoyl peroxide[56, 57] and apparently not the case with di-*tert*-butyl peroxide and ABN[58]. In pure monomer, induced decomposition is greatly reduced. However, in experiments which vary the monomer concentration, this complication should be remembered and avoided if possible.

ABN is free of both of the above complications and, in addition, is readily available and easily purified. Its rate of decomposition may be measured by nitrogen evolution[59] or spectrophotometrically[60]. As a consequence, ABN is perhaps the most popular choice of a model initiator for free-radical polymerization experiments in the temperature range 60 to 80° where its half-life varies from thirty to two hours. It is interesting to note that while ABN was synthesized as early as 1896[61], the first report of its use as a polymerization initiator appeared in 1949[59]. Since that time it has not only been found useful for research purposes, but has been widely used as an industrial initiator.

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[56] K. Nozaki and P. D. Bartlett, *J. Am. Chem. Soc.*, *68*, (1946).

[57] W. E. Cass, *J. Am. Chem. Soc.*, *68*, 1976 (1946).

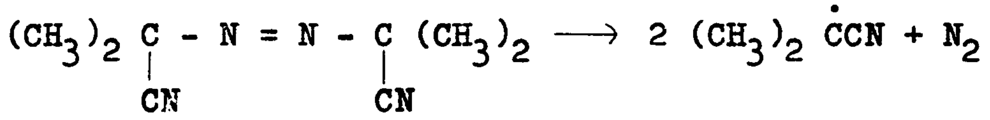
[58] C. Walling, "Free Radicals in Solution", pp. 470, 512, John Wiley and Sons, Inc., New York (1957).

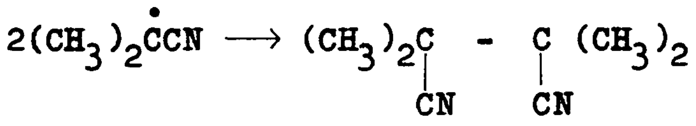
[59] F. M. Lewis and M. S. Matheson, *J. Am. Chem. Soc.*, *71*, 747 (1949).

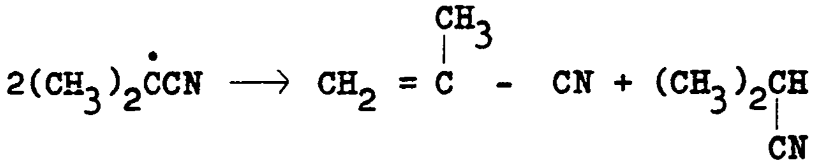
[60] M. Talat-Erben and S. Bywater, *J. Am. Chem. Soc.*, *77*, 3712 (1955).

[61] J. Theile and K. Heuser, *Ann.*, *290*, 1 (1896).

ABN, when decomposed in an inert solvent in vacuo, gives off nitrogen quantitatively and in carbon tetrachloride gives yields of up to 96 per cent tetramethylsuccinonitrile[62] (RR). A careful product study of this reaction in toluene by Bickel and Waters[63] revealed 84 per cent RR, 3.5 per cent isobutyronitrile, and 9 per cent of a product assigned the structure 2,3,5-tricyano-2,3,5-trimethylhexane. This is consistent with Steps 3, 4, and 5 of the following mechanism:

(3)

$$(CH_3)_2\underset{CN}{\underset{|}{C}} - N = N - \underset{CN}{\underset{|}{C}}(CH_3)_2 \longrightarrow 2\,(CH_3)_2\dot{C}CN + N_2$$

(4)

$$2(CH_3)_2\dot{C}CN \longrightarrow (CH_3)_2\underset{CN}{\underset{|}{C}} - \underset{CN}{\underset{|}{C}}(CH_3)_2$$

(5)

$$2(CH_3)_2\dot{C}CN \longrightarrow CH_2 = \overset{CH_3}{\overset{|}{C}} - CN + (CH_3)_2\underset{CN}{\underset{|}{CH}}$$

Schulz and coworkers[64, 65] studied the effect of variation of initiator and monomer concentrations on the rate of

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[62] G. S. Hammond, J. N. Sen, and C. E. Boozer, J. Am. Chem. Soc., 77, 3244 (1955).

[63] A. F. Bickel and W. A. Waters, Rec. trav. chim., 69, 1490 (1950).

[64] G. V. Schulz and E. Husemann, Z. phys. Chem., B39, 246 (1938).

[65] G. V. Schulz and F. Blaschke, Z. phys. Chem., B51, 75 (1945).

polymerization of styrene and methyl methacrylate and found Equation 6 to hold. They interpreted this relation to mean

$$(6) \quad R_p = \text{constant} \times (I)^{\frac{1}{2}}(M) \left[\frac{K\ (M)}{1+K(M)} \right]^{\frac{1}{2}}$$

that a complex between monomer and initiator was formed which lead to initiation of polymerization with K equal to the equilibrium constant for formation of this complex. In 1945 Matheson[66] criticized this view from two standpoints. One, the values of K determined for a benzoyl peroxide-styrene complex implied appreciable concentrations of complex, yet there was no independent evidence for the existence of such a complex. Two, the values of K increased with temperature. Matheson suggested that the initiator decomposed to give a pair of "caged" free-radicals in analogy to similar considerations[67] advanced for reactive fragments formed in photolysis. The term "caged" means that the separation of the reactive intermediates in solution is diffusion controlled so that there exists the possibility that these intermediates would react with each other before diffusing apart. In the presence of a low concentration of a radical scavenger, such as a monomer molecule, appreciable amount of primary recombination

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[66] M. S. Matheson, J. Chem. Phys., 13, 584 (1945).

[67] J. Franck and E. Rabinowitch, Trans. Faraday Soc., 30, 120 (1934).

might take place. However, as the concentration of monomer increased, this "inefficiency" in initiation could be decreased. Matheson considered three possible reactions.

I. Decomposition of the initiator, I, to give a pair of caged radicals, $\overline{2R\cdot}$.

(7) $$I \xrightarrow{k_d} \overline{2R\cdot}$$

II. A primary recombination of the caged pair to give either I or I', an isomer of I or to give both I and I'. I' may be either stable or unstable.

(8) $$\overline{2R\cdot} \xrightarrow{k_c} \text{I or I' or both}$$

III. Reaction of monomer with a caged pair to two "free" free radicals which would be capable of adding more monomer units and undergoing normal termination.

(9) $$M + \overline{2R\cdot} \xrightarrow{k_{c''}} M\cdot + R\cdot$$

Applying the steady state approximation to these three equations and using the usual propagation step of M• adding to M to give M• with bimolecular termination of M•, Matheson obtained an equation identical in form to Equation 6 of Schulz with $\frac{k_{c''}}{k_c}$ replacing K. The observed temperature dependence of K would fit with this mechanism certainly. In 1951 Mayo, Gregg and Matheson[68] reported unpublished melting point data

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[68] F. R. Mayo, R. A. Gregg, and M. S. Matheson, *J. Am. Chem. Soc.*, *73*, 1691 (1951).

of Mr. D. M. Alderman for the binary system benzoyl peroxide-styrene and found no evidence for complex formation.

By using the estimates of Franck and Rabinowitch[67] of the rates of diffusion away from each other of caged radical pairs, and the values of the absolute rate constants for the propagation and termination steps in polymerization as determined by the non-steady-state method[69], Flory[70] argued that the rate of addition of a radical to monomer was too slow to compete with the diffusion out of the cage of one member of a caged pair. Among other things, Flory assumed that monomer did not affect the rate of separation of caged radicals by diffusion. On this basis, the expected variations of efficiency with monomer concentration from Matheson's mechanism[66] (Equations 7, 8 and 9) are much lower than those determined by Schulz and coworkers[64, 65]. Recently Noyes[71] has developed a general statistical theory of cage effects and has considered specifically the effect of scavengers[72]. His estimates of cage parameters parallel those of Flory with a more detailed and reasoned approach. He shows that, while quite modest concen-

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[69] M. S. Matheson, E. E. Auer, E. B. Bevilaequa, and E. J. Hart, J. Am. Chem. Soc., 73, 1700 (1951).

[70] P. J. Flory, "Principles of Polymer Chemistry", p. 120, Cornell University Press, Ithaca, N. Y. (1953).

[71] R. M. Noyes, J. Chem. Phys., 22, 1349 (1954).

[72] R. M. Noyes, J. Am. Chem. Soc., 77, 2042 (1954).

trations of a relatively poor radical scavenger will scavenge "free" free radicals efficiently, a scavenger with very high reactivity at high concentrations should be required to appreciably affect the cage reaction.

In 1952 evidence was found in polymerization experiments that the efficiency of radical production from ABN was less than unity in certain monomers. Breitenbach and Schindler[73] estimated an efficiency of 0.72 for ABN in styrene assuming no chain transfer. Arnett and Peterson[74] observed a value of 0.80 in styrene and 1.00 in methyl methacrylate using ^{14}C labeled initiator to count initiator fragments in the polymer.

Since ABN can yield the stable product RR upon decomposition, the above results are not surprising in view of the possibility of a cage effect. From data in the literature Walling[75] compared rates of ABN decomposition as determined by nitrogen evolution with rates determined by consumption of the stable free radicals, diphenylpicrylhydrazyl (DPPH). He found the latter to lie about 75 per cent below the former in aromatic solvents. Unfortunately, values of nitrogen evolution rate constants determined in different laboratories do not agree precisely. What is worse, a later study[62], in-

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[73] J. W. Breitenbach and A. Schindler, Monatsh., 83, 724 (1952).

[74] L. M. Arnett and J. H. Peterson, J. Am. Chem. Soc., 74, 2031 (1952).

[75] C. Walling, J. Polymer Sci., 14, 214 (1954).

dicated that DPPH exhibits variable stoichiometry in counting different radicals. Perhaps the best evidence for inefficiency in the decomposition of ABN is production of RR in the presence of radical scavengers. In 1955 Hammond, Sen, and Boozer[62] compared efficiency of radical production as measured by consumption of iodine, quantitative isolation of RR in both the presence of oxygen and iodine, and by the method of inhibition using an antioxidant of known stoichiometry and cumene as a substrate. The stoichiometry of the antioxidant was determined by product isolation and the results of all of the above methods agreed well with the exception of isolation of RR in the presence of excess I_2. Here a very low yield of RR was isolated (5 per cent compared to 55 per cent estimated inefficiency in carbon tetrachloride). The precision of these experiments was around 3 per cent and small variations in efficiency were noted for different solvents. These authors suggested that a logical alternative explanation of the inefficiency of ABN decomposition would be a competitive non-radical decomposition having perhaps a transition state close to the _cis_ azo compound.

Recent work by Bevington and coworkers[76, 77] using ^{14}C-initiator and the isotopic dilution method has shown that 10

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[76] J. C. Bevington, _J. Chem. Soc._, 3707 (1954).

[77] J. C. Bevington and N. A. Ghanem, _J. Chem. Soc._, 3506 (1956).

to 30 per cent RR is formed in the thermal decomposition of ABN in benzene in the presence of excess amounts of the stable free radicals, DPPH[76] and the stable free radical obtained by oxidation of N-(3N-hydroxyanilino-1,3-dimethylbutylidene) aniline oxide[77].

Bevington[78] has also found that similar amounts of RR are formed during the ABN initiated polymerization of styrene in various concentrations of benzene. In this study Bevington estimated the efficiency of radical production as a function of monomer concentration by two methods. In the first method he measured the rate of polymerization and the specific activity of the polymer formed. This specific activity gives the number of monomer units converted to polymer per initiator fragment, a measure of the kinetic chain length. Since the kinetic chain length is equal to the rate of polymerization divided by the rate of initiation, he could then calculate the rate of initiation. From the rate constant for the decomposition of ABN, he then calculated the efficiency. In the second method he measured the amount of RR formed. By assuming a constant proportionality (4:1) between the amount of RR found and amount of ABN which decomposed inefficiently, he was able to calculate the efficiency of radical production. He did not measure the rate of decomposition of ABN. The value

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[78] J. C. Bevington, Trans. Faraday Soc., 51, 1392 (1955).

chosen for this rate affected the efficiencies as estimated by the two methods in opposite directions. He therefore chose a value which gave the same efficiency by both methods. This value for the rate of decomposition of ABN was in good agreement with that of other workers. The results of the two methods gave a constant efficiency of 63 per cent in styrene solutions except at low monomer concentration (less than 1 M). In a previous study[79], Bevington obtained a similar demonstration of inefficiency of ABN decomposition in pure styrene.

In 1955, Talât-Erben and Bywater[80, 81] discovered and identified an intermediate in the decomposition of ABN. This intermediate resulted from the unsymmetrical coupling of two cyano propyl radicals, R•, to give dimethyl-N-(2-cyano-2-propyl)-ketenimine (RR'), V.

$$(CH_3)_2C = C = N - C(CH_3)_2CN$$

V

This discovery clarifies the course of ABN decomposition, but necessitates a rather complicated mechanism. Ascribing

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[79] J. C. Bevington, "Simposio Internationale di Chimica Makromoleculare", p. 3, S.p.A. Arti Grafiche Penetto and Petrelli, Rome (1954).

[80] M. Talât-Erben and S. Bywater, J. Am. Chem. Soc., 77, 3710 (1955).

[81] Ibid., p. 3712.

the inefficiency in radical production to caged pairs of radicals, $\overline{2R\cdot}$, one must consider in addition to Equations 10, 11, 13, Equations 12, 14, 15, 16, 17, and 18.

(10) $ABN \longrightarrow \overline{2R\cdot}^{*}$

(11) $\overline{2R\cdot}^{*} \longrightarrow RR$

(12) $\overline{2R\cdot}^{*} \longrightarrow RR'$

(13) $\overline{2R\cdot}^{*} \longrightarrow 2R\cdot$

(14) $RR' \longrightarrow \overline{2R\cdot}$

(15) $\overline{2R\cdot} \longrightarrow RR$

(16) $\overline{2R\cdot} \longrightarrow RR'$

(17) $\overline{2R\cdot} \longrightarrow 2R\cdot$

(18) $2R\cdot \longrightarrow \overline{2R\cdot}$

Here the possibility that the cage parameters of two geminate radicals may differ when the parent is ABN or RR' is taken into account by denoting the "cage" from the decomposition of ABN by $\overline{2R\cdot}^{*}$.

Shortly after Talât-Erben and Bywater[80, 81] published their results, Roy, Nash, Williams, and Hamill[82] published

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[82] J. C. Roy, J. R. Nash, R. R. Williams, and W. H. Hamill, J. Am. Chem. Soc., 78, 519 (1956).

a study of the consumption of iodine in the photochemical decomposition of ABN and confirmed iodine consumption experiments of Hammond and coworkers[62] in the thermal decomposition of ABN. They repeated the thermal studies because they found that the photochemical efficiency of radical production was a monotonic increasing function of iodine concentration even at high iodine concentrations in contrast to the results in the thermal experiments where the efficiency at high iodine concentrations was independent of iodine concentration. They took this as evidence that the thermal decomposition went through a non-radical process. It should be noted that in order to make this proposal, they had to assume RR' did not react with iodine.

Subsequent to this work, Trapp[83] succeeded in isolating and characterizing RR'. He proceeded to do a careful and systematic investigation of its rate of formation and rate of decomposition in various solvents. He found that iodine, mercaptans and water reacted with it and, in fact, used its reaction with iodine as one of three independent estimates of the purity of the compound. He used quantitative infrared determinations to follow RR' concentration in his rate studies since the ketenimine has a strong absorption band at 2020 cm^{-1}. Very few organic compounds absorb in this spectral

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[83] O. D. Trapp, Unpublished Ph.D. Thesis, Iowa State College Library, Ames, Iowa (1957).

region. He also showed that RR' initiated the polymerization of styrene and, by comparing the rates of polymerization of RR' and ABN in pure styrene, he obtained an estimate of the relative efficiencies of the two initiators. Using this data, a comparison of the initial rates of formation of RR' from ABN with the efficiency of ABN, the value of 5 per cent yield of RR in the presence of excess iodine, and data for the rate of decomposition of ABN previously determined by Hammond and coworkers[62], Trapp showed that the yield of RR' resulting from the coupling of cyanopropyl radicals in the ABN "cage" was considerably larger than that assigned to the same unsymmetrical coupling in the RR' "cage". Such a result is not surprising as one would expect the "cages" to be different because a nitrogen molecule is present in one and not the other. Since the difference was large, Trapp suggested that the mechanism for the decomposition of ABN might involve the breaking of only one bond to nitrogen to give an azyl radical, $R - N = N\cdot$, and a cyanopropyl radical, rather than simultaneous breaking of two bonds to give two cyanopropyl radicals and nitrogen as is usually suggested for the decomposition of ABN. It should be noted that this mechanism is clearly distinct from a similar one suggested by Arnett[84] to explain his low efficiencies of radical production in some monomers.

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[84] L. M. Arnett, J. Am. Chem. Soc., 74, 2027 (1952).

Arnett suggested that such an azyl radical could initiate polymerization with 100 per cent efficiency whereas a cyanopropyl radical was less efficient towards some monomers. The rough agreement between rates of initiation estimated by molecular weight methods and nitrogen evolution in styrene argues against Arnett's mechanism as one might expect nitrogen to be incorporated in the polymer with azyl radicals. Finally, Trapp carried out an investigation of the decomposition of ABN in liquid bromine. He found that the rate of decomposition was no different than one usually observes upon change of solvents with ABN and the reaction produce no RR. This information suggests strongly that the production of RR in the decomposition of ABN is not due to a non-radical process.

Since Trapp's work, Neff[85] has decomposed RR' in the presence of oxygen. If oxygen acts as a simple scavenger, Step 18 of the above mechanism for the decomposition of RR' is eliminated. Thus if one obtained an increased rate of disappearance of RR' in the presence of oxygen, one could hope to estimate the extent of this reaction. Simultaneously Neff carried out a program of quantitative isolation of yields of RR from RR' both in the presence of oxygen and under nitrogen. The formation of substantially greater amounts of RR

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[85] D. L. Neff, Unpublished M.S. Thesis, Iowa State College Library, Ames, Iowa (1958).

in the presence of oxygen from RR' than from ABN is further confirmation of Trapp's mechanism involving unsymmetrical decomposition of ABN. Unfortunately the increased rate in Neff's work turned out to be due to an induced decomposition of RR' by oxygen (or peroxy radicals).

Most of this data fits into an ordered scheme of caged reactions. Noyes[86] has suggested that "hot" radicals formed in the case of ABN and not in RR' could account for the difference found in the primary yields of RR and RR' from the two initiators. The data of Roy and coworkers[82] do not fit and while it suggests several possibilities, they all point to a re-examination of the photochemical problem.

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[86] R. M. Noyes, Columbia University, New York, N.Y. Private communication to Prof. G. S. Hammond, Iowa State College, Ames, Iowa.

EXPERIMENTAL

Apparatus

Constant temperature baths

Six constant temperature baths were used in this investigation. Two of these baths used in the preliminary dilatometric investigations were of conventional design. The containers were 12 inch by 12 inch pyrex battery jars filled with either water or mineral oil (Superla White, No. 21, U.S.P. Heavy, Standard Oil). At the temperature of these investigations (70°) the mineral oil was found to be fairly color stable and gave better temperature control than did water. Two knife-type immersion heaters (Central Scientific Co.) were used as constant heat sources. One heater was adjusted with a Variac such that the temperature of the bath was slightly lower than the desired temperature. A high-speed direct-drive stirring motor (Talboys Instrument Corp.) with a single propeller was used as a stirrer. A Bronwill Thermoregulator-Thermometer (Chicago Apparatus Co.) connected to a Fisher-Serfass Electronic Relay (Fisher Scientific Co.) controlled the intermittent heating element which was a 100 watt light bulb painted black. The thermoregulator was adjustable over the temperature range 0 - 100° by rotation of a small magnet. The temperature control of these two baths was ± 0.05°.

A third constant temperature bath, used for all experiments at 62.5°, was the same as the above baths except that it was of larger capacity and consequently used a larger stirring motor. It was set up by Dr. O. D. Trapp and has been described elsewhere[87].

Two constant temperature water baths were used with the gas apparatus and were set up by Dr. S. K. Liu[88] of these laboratories. The high temperature bath (60-70°) employed knife heaters both as constant and intermittent heaters. A Bronwill Thermoregulator-Thermometer was connected to a Precision Relay (Precision Scientific Co.). Temperature control was ± 0.05°. The 25° bath which supplied water to the water jackets of the gas burettes was of 45 gallon capacity and used the same equipment as described above with the exception that a "Red-Top" Mercury Thermoregulator (Central Scientific Co.) was used with this bath. Stirring of the high temperature bath was accomplished by a High-Variable Speed Motor (Eastern Industries) and stirring of the 25° bath was accomplished by an Easy Pump (Easy Industries). In addition, during a run each bath was stirred by a pump of the same capacity as the above Easy Pump.

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[87] O. D. Trapp, Unpublished Ph.D. Thesis, p. 24, Iowa State College Library, Ames, Iowa (1957).

[88] Present address, Research Laboratories, Monsanto Chemical Co., St. Louis, Missouri.

The sixth bath was constructed of stainless steel with the exception of one side into which was built a 14 inch by 30 inch plate glass window. The bath was of 45 gallons capacity and was filled with mineral oil. All dilatometric runs starting with Run 1 were carried out using this bath which permitted complete immersion of the dilatometer. A Precision Micro-Set Differential Range Thermoregulator (Precision Scientific Co.) was connected to a Fisher-Serfass Relay which controlled a 250 watt infrared bulb for intermittent heat. Several knife heaters were used for constant heaters. Two High Speed Precision Motors (Precision Scientific Co.) stirred the bath and were situated close to both the heaters and the dilatometers. Each motor was equipped with a stirrer which has three counter-pitched windmill-type impellers. These motors were initially suspended from a bar at the top of the bath. However, their vibration complicated some runs (cf. Run 50) so that they were later completely isolated mechanically from the bath by a brace between an adjacent desk and a large pipe nearby. Temperature control was ± 0.005° and was uniform to this precision throughout the region where the dilatometers were situated.

Dilatometer design

The dilatometer design was essentially that employed by Bartlett and Kwart[89], with the exception that the reaction cell was placed on the same side of the dilatometer as the monomer degassing reservoir. This change facilitated cleaning the dilatometers. Also, the bottom of the monomer degassing reservoir was flattened in order to permit the contents of this reservoir to be stirred effectively with a magnetic stirrer. Additional small reservoirs were added to the dilatometer for runs in which initiator or inhibitor were to be kept separated from the monomer during degassing. While the volume cell of each of the dilatometers contained roughly 20 ml., the shape of the volume cell varied. In the first three dilatometers constructed, the height of the volume cell was approximately equal to its diameter. In later dilatometers, the height was always made at least two times the diameter. The data on values of capillary diameter, volume of volume cell, and approximate size of volume cell are tabulated for the individual dilatometers in the Results Section of this thesis. The length of the calibrated capillary pairs in each dilatometer was around 8 inches. One 12/30 standard taper female joint connected the dilatometer to the vacuum manifold.

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[89] P. D. Bartlett and H. Kwart, J. Am. Chem. Soc., 72, 1051 (1950).

In preliminary experiments (runs made prior to Run 1), in which the large-windowed constant temperature bath was not used, a slight modification was made in the above dilatometer design[89]. Water condensers were placed at the two positions between the monomer reservoir and the capillaries. In these experiments both the capillaries and the monomer reservoir were above the constant temperature bath whereas the volume cell was immersed in the bath. Without the condensers, excess monomer distilled from the monomer reservoir, condensed in the upper portions of the dilatometer, and drained in part into the capillaries. The condensers reduced the extent of this process to such an extent that induction periods could be identified with precision although rates of polymerization could not be determined. These results were in good agreement with later runs.

Cathetometer

A precision cathetometer (Gaertner Scientific Corp.) was used to make all dilatometric measurements. This cathetometer has a precision of ± 0.005 cm. The cathetometer could be placed as close as 12 inches to the dilatometer capillary and still remain in focus.

Dilatometer support

The dilatometer support was anchored to the bottom of the 45 gallon oil bath (see subsection on Constant Temperature Baths) at the drainage hole. This support was machined from brass in the shape of a "T" (from the top) 6 inches by 11 inches and its thickness was 1.5 inches. Two vertical 0.5 inch steel rods, rigidly attached to the support, were secured to a crossbeam at the top of the bath after leveling of the support. The brass support contained three tapered holes (0.75 inch at top to 0.56 inch at bottom) which were keyed to accept a rectangular slot. Three 0.5 inch brass rods with male-tapered plugs at the bottom, with a rectangular slot running the length of the taper, which fit the tapered holes in the support were cut of length such that 6 inches of rod rose above the level of the bath. These rods, with the machined taper at the bottom end, could be removed and replaced in the dilatometer support reproducibly. The tapered plug not only gave "good" mechanical stability but permitted thermal expansion without danger of freezing when the cold rod was inserted into the support with the bath at 70°.

Each machined rod had attached to it two Micro Clamps (No. 2C, Arthur H. Thomas Co.). The clamps supported the dilatometer at two positions on one of the capillaries. These clamps are adjustable such that the dilatometer capillary could be positioned vertically. The initial lining up was done while the bath was still empty of oil by sighting with the cathetometer. A weighted thread was used as a plumb line and sightings were taken from two positions (90° apart with respect to the center dilatometer) successively until the capillaries were determined to be vertical.

Calibration of the dilatometers

Six 8 inch lengths of 1.00 ± 0.01 mm. (inner diameter) precision bore capillary tubing (Fisher and Porter Co.) were checked for uniformity of bore by measuring the length of a 1 cm. thread of mercury at 20 different positions along each capillary length. The uniformity of bore was within the manufacturer's specification of ± 0.76 per cent.

Two dilatometers constructed with precision bore tubing and three dilatometers constructed with ordinary stock capillary tubing were calibrated using the method of Bartlett and Kwart[89]. Mercury was first placed in the monomer reservoir, the dilatometer was evacuated with a fore pump, and the mercury was degassed by heating with a low Bunsen-burner flame. After the mercury cooled, the volume cell was filled with mercury and the system was returned to atmospheric pressure. This procedure eliminates air pockets in the volume cell. The excess mercury in the rest of the dilatometer was removed by using a length of plastic insulation ("spaghetti") for very fine wire which was connected to a mercury trap and an aspirator. The method of Bartlett and Kwart[89] consists of raising the temperature over a small interval (2°) at several different temperatures. From the weight of mercury in the dilatometer, the expansion coefficient of mercury, the increase in height of the mercury in the capillary, and the temperature difference, the area of the capillary was calculated at various positions of the capillary. Measurements with the five dilatometers were done at five different temperatures (which covered at least half of the capillary range for these dilatometers). The averaged values for these dilatometers are given in the Results Section.

Agreement with the manufacturer's specification was very good. Therefore, later dilatometers were simply weighed with mercury to determine their volume, and the manufacturer's value for the capillary diameter was used directly.

Finally several of the above dilatometers were compared by polymerizing the same solution of azo-bis-isobutyonitrile in styrene in them at 50°. At this temperature the decomposition of initiator is negligible so that the rates of polymerization should indicate both the relative area to volume ratios for the dilatometers and the uniformity of bore of the dilatometer. The results of these experiments are also given in the Results Section of this thesis.

High vacuum systems

In preliminary experiments, solutions were degassed on a vacuum system described by Tanaka[90]. The vacuum obtained during degassing was only 10^{-3} to 10^{-4} mm. mercury. While all of the preliminary experiments (non-numbered runs and in general runs not reported in this thesis) were carried out in this manner, the results indicated that better degassing was desirable.

All numbered dilatometer runs were degassed on a vacuum system built by Dr. W. P. Baker[91] which consisted of a Megavac fore pump (Central Scientific Co.), a two stage oil diffusion pump (Type GF-20W, Distillation Products Industries) which used for pump oil Octoil-S (Consolidated Vacuum Corp.), and a Cold Cathode Ion Gauge (Miller Laboratories). The system was equipped with only one high-vacuum stopcock (25 mm, three-way) and one large trap on the high vacuum side of the manifold. This system routinely gave pressures of less than 10^{-6} mm. mercury. Mr. W. M. Moore[92] placed six high-vacuum stopcocks (6 mm., right angle side arm) on the manifold which

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[90] J. A. Tanaka, Unpublished Ph.D. Thesis, p. 76, Iowa State College Library, Ames, Iowa (1956).

[91] Present address, Film Division, E. I. DuPont de Nemoirs and Co., Experimental Station, Wilmington, Delaware.

[92] Present address, Chemistry Department, Iowa State College, Ames, Iowa.

permitted degassing six dilatometers simultaneously. The 6 mm. size stopcock was chosen to match the inner diameter of a 12/30 standard taper joint used with the dilatometers.

Gas apparatus

The gas apparatus was essentially the same as the one described by Boozer, Hammond, Hamilton, and Sen[93] and was built by Dr. S. K. Liu[94].

Potentiometer and electrodes

A Beckman Model G pH meter was used with a glass and standard calomel electrodes for the potentiometric titrations.

Reaction tubes

Reaction tubes were made by constricting Pyrex culture tubes (25 x 150 mm.) two inches from the mouth. All tubes were left overnight in the annealing oven of the Chemistry Glass Shop after constriction.

Thermistor measurements

Of several thermistors (Gulton Industries, Inc.) tried, a very small one enclosed in a glass probe proved most useful

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[93] C. E. Boozer, G. S. Hammond, C. E. Hamilton, and J. N. Sen, *J. Am. Chem. Soc.*, *77*, 3233 (1955).

[94] Present address, Research Laboratories, Monsanto Chemical Co., St. Louis, Missouri.

and was used in all temperature comparisons with thermistors. Its resistance at 70° was 469 ohms and its temperature coefficient was 3 per cent per degree. A simple Wheatstone bridge made from three 999.9 ohm decade boxes (Leeds and Northrup Co.) was used. A temperature change of 0.1° corresponded to 1.2 ohm. Since temperature comparisons between two baths on opposite sides of the room were made, the thermistor was connected to the bridge with 20 feet of "Zip" cord. No complications from inductance linkage with stray magnetic fields were encountered.

Chemicals

Acetic acid

Glacial acetic acid (Analytic Reagent, Mallinckrodt Chemical Works) was used without further purification.

Acetonitrile

Acetonitrile (Purified Grade, Fisher Scientific Co.) was used directly without further purification.

Anthracene

Anthracene (Eastman White Label, Eastman Kodak Co.) which had been chromatographed with untreated alumina and then sublimed by Dr. S. K. Liu[95] was used directly.

Azo-bis-isobutyronitrile

Azo-bis-isobutyronitrile (White Recrystalized Grade, Westville Laboratories, Monroe, Connecticut) was recrystallized twice from methanol by saturating a solution of methanol at room temperature and cooling the solution to 5° overnight. The large translucent needles (1-2 cm. in length) were dried and stored over calcium chloride *in vacuo* at 5° in the dark. The melting point was 101 - 102° (uncorrected) with decomposition. Azo-*bis*-isobutyronitrile (ABN) used directly without recrystallization will be designated as from source 0 and ABN recrystallized as above will be designated as from source 1. ABN from source 1 was dissolved in a small quantity of acetone and poured into a large volume of Skelly A with rapid stirring. Two such crystallizations gave fine crystals which will be designated as ABN from source 2. ABN, the purification of which is described elsewhere[96], was obtained from Trapp and will be designated as from source 3-T.

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[95] Present address, Research Laboratories, Monsanto Chemical Co., St. Louis, Missouri.

[96] O. D. Trapp, Unpublished Ph.D. Thesis, p. 27, Iowa State College Library, Ames, Iowa (1957).

1,2-Benzanthracene

1,2-Benzanthracene (Eastman White Label, Eastman Kodak Co.) was used without further purification, melting point, 159-160° (uncorrected).

Benzene

Benzene (Analytical Reagent, Thiophene Free, Mallinckrodt Chemical Works) was used directly without further purification in all experiments in benzene solution with the gas apparatus and with the sealed tube kinetic runs. For benzene solutions in the dilatometric experiments, the benzene was mixed (by high speed stirring) with successive portions of concentrated sulfuric acid until the sulfuric acid layer was colorless, washed with a dilute aqueous sodium bicarbonate solution, was washed with two portions of distilled water, and was dried over calcium chloride. It was then distilled on a 30 (actual) plate Oldershaw Column at a reflux ratio of 1:22. The middle fraction, which distilled at 80.2° was used directly.

Bromine

Bromine (Reagent Grade, Allied Chemical and Dye Corp.) was used directly without further purification.

Carbon tetrachloride

Carbon tetrachloride (Reagent Grade, Fisher Scientific Co.) was used directly without further purification unless otherwise noted. A portion of the carbon tetrachloride was specially purified (to eliminate the possibility of carbon disulfide contamination) for use as a solvent for ultraviolet spectra. It was refluxed over mercury for four hours, washed four times with concentrated sulfuric acid, refluxed two hours each with three portions of 5 per cent sodium hydroxide, washed twice with water, dried over calcium chloride, and distilled on a 30 (actual) plate Oldershaw Column at a reflux ratio of 1:17. The boiling point range was 76.4 to 76.8°. The ultraviolet cut off of purified material was the same (3580Å) as that of carbon tetrachloride which was not subjected to this treatment.

Chloranil

Chloranil (Eastman White Label, Eastman Kodak Co.) was recrystallized twice from glacial acetic acid and dried *in vacuo* over sodium hydroxide pellets for several days until all odor of acetic acid was gone, melting point, 295 - 297° (uncorrected) *in vacuo*.

Chrysene

Chrysene (Eastman White Label, Eastman Kodak Co.) when recrystallized from benzene gave light yellow-green plates. These melted at 254-260° (uncorrected) on both the first and second recrystallizations. Chrysene from the second recrystallization was used in this work.

Cumene

Cumene (Eastman White Label, Eastman Kodak Co.) was washed with concentrated sulfuric acid once, washed with dilute aqueous sodium bicarbonate solution, washed twice with water and dried over anhydrous (granular) sodium sulfate. It was then distilled at atmospheric pressure under nitrogen at a reflux ratio of 1:2 on a small 30 inch vacuum-jacketed column packed with Metal Helices (Podbielniak, Inc.). Purified cumene gave only one peak on a gas-phase chromatograph[97]. It was stored under nitrogen and used within two weeks.

Cyclohexane

Cyclohexane (99 mole per cent Minimum, Pure Grade, Phillips Petroleum Co.) was used without further purification for all work except as a solvent for ultraviolet spectra. Its

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[97] Private communication, Mr. W. M. Moore, Iowa State College, Ames, Iowa.

cut off was at 2350Å as compared to the cut off of 2200Å for spectral grade (Spectral Grade, Phillips Petroleum Co.) cyclohexane.

Di-t-butyl-p-cresol

Di-t-butyl-p-cresol was recrystallized once from ethanol and gave light yellowish plates, melting point, 69.5-71.0° (uncorrected). Further recrystallization from ethanol did not remove the color or raise the melting point. The compound was used after one recrystallization.

2,5-Dichloroquinone

2,5-Dichloroquinone (Eastman White Label, Eastman Kodak Co.) was recrystallized three times from ethanol and dried *in vacuo*. The product from the third recrystallization melted at 159-162° (uncorrected) *in vacuo*.

2,6-Dichloroquinone

2,6-Dichloroquinone (Eastman White Label, Eastman Kodak Co.) was recrystallized twice from ethanol and dried *in vacuo* before use, melting point, 120.5-121.5° (uncorrected) *in vacuo*.

Dimethyl-N-(2-cyano-2-propyl)-ketenimine

Dimethyl-N-(2-cyano-2-propyl)-ketenimine (RR') was prepared by Trapp's method[98] using azo-bis-isobutyronitrile from source O. A one-plate distillation, using a fore pump and a simple Claisen head, yielded several progressively yellower fractions A, B, C, D from the crude yellow product of the initial preparation. Fraction D was distilled using a small Spinning Band Column (Nexter and Faust, Inc.) and a fore pump. Two colorless fractions, SB-1 and SB-2 were obtained. All yellow fractions were combined with a yellow fraction donated by O. D. Trapp and distilled on the Spinning Band Column using the vacuum system built by Tanaka (see Apparatus Subsection). Distillation at 30° yielded five colorless fractions numbered 1, 2, 3, 4, 5. These latter fractions together with a colorless fraction of RR' generously donated by Mr. D. L. Neff[99] (designated as N-2) were used for most experiments in this investigation. Sample SB-2 (0.3 ml.) melted at 15.1-16.7° in a cold bath whose temperature rose at the rate of 1° per 5 minutes. Index of refraction of both yellow (C) and colorless (SB-2) fractions was the same ($n^{25.0} = 1.4470$). Samples

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[98] O. D. Trapp, op. cit., p. 31.

[99] Present address, Research Laboratories, The Kendall Corp., Chicago, Illinois.

were stored at -20° under nitrogen. Estimation of purity is described later in this section of this thesis.

Dioxan

Dioxan (Technical Grade, Allied Chemical and Dye Corp.) was used without further purification.

Diphenylpicrylhydrazyl

Diphenylpicrylhydrazyl (DPPH) was prepared from picryl chloride (Eastman White Label, Eastman Kodak Co.) and 1,1-diphenylhydrazine hydrachloride (Eastman White Label, Eastman Kodak Co.) using the procedure of Goldschmidt and Renn[100]. The crude product was recrystallized at least three times from benzene. Care was taken to heat the solution only long enough to completely dissolve the DPPH. Large crystals usually appeared after one-half hour of slow cooling. This material was used immediately after preparation for one set of runs only.

Other experiments used DPPH prepared in 1955 by Dr. Sen of these laboratories and which had been stored in the dark at room temperature for two years. This DPPH had an extinction coefficient of 28.3 liters gm^{-1} cm^{-1} at 5300Å in chloroform. After drying at 80° *in vacuo* for 15 hours the extinc-

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[100] S. Goldschmidt and K. Renn, *Ber.*, *55*, 628 (1922).

tion coefficient rose to 29.0 liter gm.$^{-1}$ cm.$^{-1}$. Lyons and Watson[101] present evidence that this effect is due to the presence of solvent complexed with DPPH. They report the maximum extinction coefficient is 32.2 liters gm.$^{-1}$ cm.$^{-1}$ at 5325Å for chloroform. DPPH was recrystallized as above and concentrations were calculated assuming a 1:1 (or 1:3) stoichiometry between DPPH and benzene (or chloroform)[100]. The melting point before recrystallization was 134-136° (uncorrected) with decomposition. Its melting point (uncorrected) with decomposition was 139-141° after the first recrystallization from benzene and 142-143° after the third recrystallization.

Fluoranthene

Fluoranthene (95 per cent Minimum Purity, Reilly Tar and Chemical Corp.), which had been recrystallized from ethanol was obtained through the generosity of Dr. S. K. Liu[95] and gave a melting point of 109.0-110.5° (uncorrected).

Hydrobromic acid

Hydrobromic acid (48 per cent, Eastman White Label, Eastman Kodak Co.) was used without further purification.

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[101] J. A. Lyons and W. F. Watson, J. Polymer Sci., 18, 141 (1955).

Mercury

Mercury (Redistilled, N. F., Fischer Scientific Co.) was used without further purification.

Perchloric acid

Perchloric acid (70 per cent C. P., The G. Frederick Smith Chemical Co.) was used without further purification.

Phenanthrene

Phenanthrene which had been chromatographed on untreated alumina and resublimed was obtained through the generosity of Dr. S. K. Liu[95].

Styrene

Styrene (Eastman White Label, Eastman Kodak Co.) was washed with four portions of 5 per cent aqueous sodium hydroxide solution, two portions of water, and dried over calcium chloride. It was then distilled under nitrogen on a simple 6 inch Vigreaux column and used immediately. This procedure was used in all runs unless otherwise noted. The styrene thus distilled gave only one peak on a gas phase chromatograph[97], was colorless, and gave no precipitate upon addition to methanol.

Tetracyanoethylene

Tetracyanoethylene was obtained through the generosity of Dr. B. C. McKusick[102]. It was a yellowish white powder which was stored in a calcium chloride desiccator at room temperature and was used as received.

Tetramethylsuccinonitrile

Tetramethylsuccinonitrile which had been recrystallized and resublimed was obtained through the generosity of Mr. D. L. Neff[99].

Dilatometric Runs

Dilatometers were cleaned prior to use either by leaving them overnight in the annealing oven of the Chemistry Glass Shop or by filling them completely with a 3:1, sulfuric acid: nitric acid mixture, immersing them in a hot acid bath for at least two hours, rinsing them four times with water, rinsing them once with concentrated aqueous ammonium hydroxide solution, rinsing them four more times with water, and heating them for several hours in a vacuum drying oven at 100°.

In most runs, additives (initiator, inhibitor) were weighed into a 50 ml. volumetric flask. Liquids were weighed

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[102] Central Research Department, E. I. DuPont de Nemoirs and Co., Experimental Station, Wilmington, Delaware.

added from a tared hypodermic syringe and non-reactive additives were weighed using an aluminum weighing scoop. The required amount of styrene was pipetted into the volumetric flask which was then diluted to volume with benzene. The solution was then transferred from the flask to the monomer reservoir with a 50 ml pipette. In runs in which the additives were to be kept separate from monomer during the degassing process, the additives were weighed into the small reservoirs on the dilatometers and the tops of these reservoirs were sealed. Monomer and benzene were then pipetted into the monomer reservoir. In either case, dilutions carried out in air for a series of six runs took one to two hours to complete.

The dilatometers were attached to the vacuum system, frozen with liquid nitrogen, and evacuated using the fore pump. No less than three freeze-thaw cycles, in which the diffusion pump was used during the freeze cycle, were used to degas the dilatometers. In some experiments the mixture was stirred during the thaw cycle with a small nail enclosed _in vacuo_ in glass. This nail was placed in the monomer reservoir (prior to the run) and was rotated with a high speed magnetic stirrer. In all runs in which degassing was done with the oil diffusion pump, the pressure at the last freeze step when the dilatometer was sealed-off was less than 10^{-6} mm. mercury. In many runs on this system the requirement for sealing-off was that the surge pressure on the last freeze cycle be no greater than 2 x 10^{-6} mm. mercury. Dilatometers were stored in the dark with the monomer (and additive) reservoirs immersed in a dry ice-acetone mixture.

Prior to the run, the contents of the dilatometer were warmed to room temperature, mixed thoroughly, and poured into the volume cell (by tipping the dilatometer). The dilatometer was clamped to the dilatometer-support rod and placed in the bath. The time at which the dilatometer was placed in the bath was taken as zero time for the run. During the first ten minutes of the run the dilatometer was shaken (by means of the removable support rod) from time to time while still immersed in the bath. After ten minutes time, if the level of the liquid in the capillaries was not in a convenient range, the level was adjusted by pouring monomer out of or into the capillaries. Cathetometer readings were taken which included a reference point on the bath, a reference point on the dilatometer, and the liquid level. Temperature constancy was recorded during the runs by reading a Beckmann thermometer.

After a run, the dilatometer was opened and rinsed free of polymer with at least four portions of technical benzene and one of acetone.

Gas Apparatus Runs

The procedure described by Boozer, Hammond, Hamilton, and Sen[103] for autoxidation runs was followed in detail. For the

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[103] C. E. Boozer, G. S. Hammond, C. E. Hamilton, and J. N. Sen, _J_. _Am_. _Chem_. _Soc_., _77_, 3233 (1955).

nitrogen evolution experiments 6 ml. of solvent were always used. The apparatus was evacuated and filled with nitrogen which was passed through a Fieser Train[104] three times prior to a run. Two stirring rates were used. "Slow" stirring rates were obtained with a Mag-Mix magnetic stirrer (Precision Scientific Co.) and produced only a modest defomation of the surface. A large horse shoe magnet attached to a high speed stirrer whose speed was controlled with a Variac gave stirring with a large vortex and was termed "fast" stirring.

In some nitrogen evolution experiments the total volume of nitrogen as well as the decrease in ultraviolet absorption of azo-bis-isobutyronitrile was measured. In all experiments in which ultraviolet measurements were to be made on the reaction mixture, Kel-F Stopcock Grease (The M. W. Kellogg Co.), a fluorocarbon grease with negligible absorption in the near ultraviolet, was used on the standard taper joints of the reaction cell. Care was taken to avoid any actual contact of the reaction mixture with these greased joints. The stirred reaction cell was degassed four times with the fore pump, returned to atmospheric pressure, and the volume was measured at 25°. The reaction cell was then disconnected from the 25° bath and connected to the high temperature bath. Zero time

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[104] L. F. Fieser, "Experiments in Organic Chemistry", p. 395, Second Edition, D. C. Heath and Co., New York (1941).

was considered as the time at which the water from the high temperature bath was started through the reaction cell. If the circulation pump (located outside of the high temperature bath) had not been pumping hot water immediately prior to starting the run, it sometimes took as long as eight or nine minutes for the bath to reach temperature equilibrium. If the pump was preheated by prior pumping, temperature equilibration could be established within two minutes. In either case the temperature of the water bath never fell more than 2 - 3° and it was felt that the 6 ml. of stirred reaction mixture equilibrated quite rapidly with respect to the above times. If the total volume of nitrogen was to be measured, the time was noted at the end of the run and the hot jacket of the reaction cell (normally connected to the high temperature bath) was connected to the 25° bath and the final volume was read. In these runs special care was taken to check for the possibility of leaks in the system. Initial and final readings were required to remain constant for at least one-half hour with constant searching by the pressure regulator. Finally, the reaction mixture was transferred quantitatively to a 25 ml. volumetric flask, diluted to volume and the ultraviolet determination was made. Initial ultraviolet absorption was calculated from measurements made with another weighed sample of azo-bis-isobutyronitrile.

Sealed Tube Runs

Thirteen sealed tubes were attached using rubber stoppers to a "pig" and were degassed with a fore pump. Either liquid nitrogen or a dry ice-acetone mixture was used for freezing the samples. Four freeze-thaw cycles were used in all cases and the samples sealed *in vacuo*.

Samples were placed in the constant temperature bath, removed at intervals, and quenched in a dry ice-acetone bath. For all runs of duration less than one hour, samples were shaken vigorously during quenching. The samples were stored under dry ice until they were opened for analysis.

Decomposition of the Ketenimine in the Presence of Oxygen and Antioxidant

Dimethyl-N-(2-cyano-2-propyl)-ketenimine (RR') and di-*t*-butyl-*p*-cresol were weighed into a 250 ml. three-necked flask which was filled with a known volume of a 2:1 mixture of carbon tetrachloride and cumene. The flask was placed in a constant temperature bath, was stirred mechanically, and was swept with oxygen every two hours. Samples were removed at intervals with a hypodermic syringe and placed in 10 ml. corked flasks which were stored either at -20° or over dry ice until the samples were analyzed for RR' by the infrared method. The above procedure was developed by Neff and is described elsewhere[105].

Temperature Determinations

Bath temperatures were set using a National Bureau of Standards thermometer. Two such thermometers agreed within 0.05° at 70°. Relative temperatures were determined both with Beckman thermometers and with a thermistor. They gave similar results although the thermistor had practically no thermal lag and was more sensitive. Because of the thermistor's small size, it was easy to adjust the temperature of the reaction cell of the gas apparatus exactly (to 0.1°) to that of a reference bath. In addition, the temperature of an unstirred styrene run was estimated for a sealed tube experiment by measuring the temperature of the reaction mixture in an unsealed tube. The reaction mixture was flushed with nitrogen prior to the determination.

Ultraviolet Measurements

Ultraviolet measurements were made with a Beckman Model DU Spectrophotometer and a Cary Model 12 Recording Spectrophotometer.

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[105] D. L. Neff, Unpublished M.S. Thesis, Iowa State College Library, Ames, Iowa (1958).

Infrared Measurements

Infrared measurements were made with the Perkin Elmer Model 13 and the Perkin Elmer Model 112 instruments. The method used was the "cell in-cell out" method described in detail by Trapp[106].

Titration of Dimethyl-N-(2-Cyano-2-Propyl)-Ketenimine

Titration with hydrobromic acid in acetic acid

Two weighed samples of about 0.1 gm. each of dimethyl-N-(2-cyano-2-propyl)-ketenimine (RR') which were dissolved in 25 ml. glacial acetic acid gave less than 0.5 ml. titer with 0.085 M hydrobromic acid in acetic acid. Another weighed 0.1 gm. sample of RR' dissolved in 25 ml. chlorobenzene gave a 2 ml. titer which corresponded to a recovery of 30 per cent. By the infrared method, the purity of this fraction assayed around 80 per cent. The visual crystal violet end point agreed with the potentiometric end point. At the end point of the titration a fine precipitate clouded the chlorobenzene solution. Tetramethylsuccinonitrile was shown to be soluble under these conditions.

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[106] O. D. Trapp, Unpublished Ph.D. Thesis, p. 47, Iowa State College Library, Ames, Iowa (1957).

Titration with perchloric acid in dioxan

Two weighed samples of about 0.1 gm. each of RR' (from the same fraction as above) were dissolved in dioxan. These two samples when titrated with 0.064 M perchloric acid in dioxan gave about 8 ml. titers which corresponded to recovery of 56.6 and 52.8 per cent RR' respectively. A crystal violet end point had to be used as the dielectric constant of dioxan was too low to permit stable potentiometric readings to be obtained. Over-titration by 100 per cent (of the above assays) with perchloric acid and immediate back-titration with 0.035 M triethylamine in dioxan gave an recovery of 56.5 per cent for a third weighed sample. Since it was desired to be able to calibrate the visual end point with a potentiometric end point, this system was abandoned.

A solution of RR' in acetonitrile permitted the potentiometric method to be used when such a solution was titrated with 0.064 M perchloric acid in dioxan. A 10 ml. aliquot of an acetonitrile solution about 0.06 M in RR' was over-titrated with 5 ml. of the perchloric acid and allowed to stand for 40 minutes. Back-titration with 0.037 M triethylamine in dioxan required 4 ml., which represents a recovery of only 26 per cent. Two 10 ml. aliquots when over-titrated (individually) with 10 ml. of perchloric acid solution and allowed to stand for 14 hours (while covered by a watchglass) assayed 75 and 74 per cent respectively. Blank perchloric acid solution when allowed to stand similar lengths of time gave the correct titer of triethylamine. The end points of the back titrated RR' solutions seemed to be slowly transient (requiring more base).

Titration with hydrobromic acid in dioxan

Using the potentiometric method, a 10 ml. aliquot from the 0.06 M solution of RR' in acetonitrile was over-titrated with 15 ml. of 0.051 M hydrobromic acid in dioxan. Back-titration after 15 minutes required 15 ml. of 0.037 M triethylamine in dioxan (28 per cent recovery). Another 10 ml. aliquot of the RR' solution over-titrated with 6 ml. of hydrobromic acid gave, by the same procedure, an assay of only 9 per cent. Leaving solutions of hydrobromic acid covered with a watchglass for a period of several hours led a decrease in titer, probably because of volatilization of the acid.

Titration with bromine in carbon tetrachloride

A 0.03 M solution of bromine in carbon tetrachloride was standardized against a standard (aqueous) sodium thiosulfate solution in the following manner. Five gm. of potassium iodide (Analytical Reagent Grade, Mallinckrodt Chemical Works) was dissolved in 30 ml. of water, 10 ml. of the bromine solution was added and the mixture was stirred for five minutes. The mixture was then titrated with standard thiosulfate solution to a starch end point. The time of stirring had no effect within the experimental scatter (± 0.4 per cent). The thiosulfate solution was standardized against potassium dichromate using the method described by Pierce and Haenisch[107].

One tenth gm. samples of a colorless RR' fraction (N-2) were weighed into three 50 ml. Erlenmeyer flasks. Each fraction was titrated directly with the standard bromine solution. The bromine solution was decolorized immediately upon addition and a distinct bromine color was observed after the end point. Since this procedure necessarily leads to an over-titration, the end point was estimated in the following manner. Bromine solution was added dropwise to a blank flask (containing the same amount of carbon tetrachloride as the over-titrated sample) until the contents of both flasks appeared visually to have the same color. The blank titration was subtracted from the titer and this correction amounted to 0.5 per cent. In a previous titration, visual estimation of the amount of excess bromine added to a sample of RR' was compared spectrophotometrically (using the Beckman Model DU at 4000Å) with a standard bromine solution of nearly the same concentration. Assuming Beer's Law to hold for solutions of bromine in carbon tetrachloride, the spectrophotometric estimate agreed with the

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[107] W. C. Pierce and E. L. Haenisch, "Quantitative Analysis", p. 244, Third Edition, John Wiley and Sons, Inc., New York, N. Y. (1948).

visual estimate of excess bromine. The results of the three assays of this fraction were 86.8, 86.8 and 86.7 per cent RR'. On the following day, quantitative infrared and ultraviolet measurements were made on this same fraction (which had been stored in the dark at -20°).

Infrared and Ultraviolet Analyses of Dimethyl-N-(2-Cyano-2-Propyl)-Ketenimine

In the present investigation, it was necessary to know quantitatively the amount of dimethyl-N-(2-cyano-2-propyl)-ketenimine (RR') in both the polymerization and the air-oxidation studies. Since the samples of RR' to be analyzed had been purified and contained only the stable isomer of RR', tetramethylsuccinonitrile, it was thought that it would be convenient to use a quantitative ultraviolet method for assay of RR' as tetramethylsuccinonitrile does not absorb in the region of the RR' peak. The infrared method, while quite specific for ketenimine, is operationally more complicated than an ultraviolet method and it was anticipated that it might be somewhat less precise.

As Trapp[108] had calibrated the infrared method by two independent chemical assays, a series of simultaneous ultraviolet and infrared measurements were made with samples of

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[108] O. D. Trapp, Unpublished Ph.D. Thesis, p. 38, Iowa State College Library, Ames, Iowa (1957).

RR'. Unfortunately, the cells which Trapp used for his work were also used for routine, qualitative, infrared analyses so that there was some uncertainty as to whether or not their calibrations were still correct. Before the calibration could be checked, the cells were destroyed. While a set of calibrated cells (Perkin-Elmer Corp.) were available for further work, it was felt that the present work could be inaccurate (in terms of Trapp's work) to an extent of perhaps 10 per cent. So, during the progress of this investigation, a number of cross calibrations of these methods were made which are shown in Table 1.

In Table 1, each entry corresponds to a separate weighed sample unless otherwise indicated. The data are arranged with respect to different fractions of RR'. Samples within the same fraction are arranged chronologically. Bulk specific absorbancy, $\bar{A}$, is the observed absorbancy divided by the weight per liter of RR' fraction (i.e. no correction for purity). Inspection of the ultraviolet data, shows that its precision within the same fraction is good (± 3 per cent scatter at most). In contrast to the ultraviolet data, the infrared data scatter around ± 5 per cent within the same fraction.

The analyses in Table 1 of the four fractions of N-2 of January 27 were made within a day of the time fraction N-2 was titrated with bromine. Assuming the latter assay was

Table 1. Infrared and ultraviolet bulk specific absorbancies for various fractions of dimethyl-N-(2-cyano-2-propyl)-ketenimine in carbon tetrachloride and cyclohexane

Fraction	Date	Bulk conc. (gm/l)	Infrared		Ultraviolet		Infrared		Ultraviolet	
			$\bar{A}_{13}$[a] (CCl_4) 2020cm^{-1}	$\bar{A}_{112}$[b] (CCl_4) 2020cm^{-1}	$\bar{A}_{DU}$[c] (CCl_4) 2850Å	$\bar{A}_{C}$[d] (CCl_4) 2850Å	$\bar{A}_{13}$[a] (C_6H_{12}[e]) 2020cm^{-1}	A_{112}[b] (C_6H_{12}[e]) 2020cm^{-1}	$\bar{A}_{DU}$[c] (C_6H_{12}[e]) 2910Å	$\bar{A}_{C}$[d] (C_6H_{12}[e]) 2910Å
1	7/5	0.601								0.980
	7/5	1.05								0.983
3	7/5	0.752								0.972
	7/18	0.888					0.376			

[a] Bulk specific absorbancy (gm.$^{-1}$) as determined with the Perkin-Elmer Model 13 (lithium fluoride prism, slit width of 0.500 mm.) using 0.948 mm. sodium chloride cells.

[b] Bulk specific absorbancy(gm.$^{-1}$) as determined with the Perkin-Elmer Model 112 (lithium fluoride prism, slit width of 0.900 mm.) using 0.948 mm. sodium chloride cells.

[c] Bulk specific absorbancy (gm.$^{-1}$) as determined with the Beckman Model DU using 1.00 cm. quartz cells.

[d] Bulk specific absorbancy (gm.$^{-1}$) as determined with the Cary Model 12 using 1.00 cm. quartz cells.

[e] Cyclohexane.

Table 1. (Continued)

Fraction	Date	Bulk conc. (gm/l)	Infrared		Ultraviolet		Infrared		Ultraviolet	
			$\bar{A}_{13}$[a] (CCl_4) $2020cm^{-1}$	$\bar{A}_{112}$[b] (CCl_4) $2020cm^{-1}$	$\bar{A}_{DU}$[c] (CCl_4) 2850Å	$\bar{A}_C$[d] (CCl_4) 2850Å	$\bar{A}_{13}$[a] (C_6H_{12}[e]) $2020cm^{-1}$	A_{112}[b] (C_6H_{12}[e]) $2020cm^{-1}$	$\bar{A}_{DU}$[c] (C_6H_{12}[e]) 2910Å	$\bar{A}_C$[d] (C_6H_{12}[e]) 2910Å
4	7/5	0.855								0.975
	8/20	1.64	0.395							
5	7/5	1.62								0.977
	7/18	2.62	0.373							
	7/18	2.05	0.345							
	7/18	1.18	0.353							
	7/18	0.820	0.376							
	7/18	2.64					0.351			
	7/18	2.03					0.365			
	7/18	1.44					0.365			
	7/18	1.02					0.368			
	7/18	0.950					0.382			
Neff[f]	10/18	1.98		0.354		1.24				

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[f] An undesignated fraction of RR' weighed out by and obtained from D. L. Neff.

Table 1. (Continued)

Fraction	Date	Bulk conc. (gm/l)	Infrared $\bar{A}_{13}$[a] (CCl_4) 2020cm^{-1}	Infrared $\bar{A}_{112}$[b] (CCl_4) 2020cm^{-1}	Ultraviolet $\bar{A}_{DU}$[c] (CCl_4) 2850Å	Ultraviolet $\bar{A}_{C}$[d] (CCl_4) 2850Å	Infrared $\bar{A}_{13}$[a] (C_6H_{12}[e]) 2020cm^{-1}	Infrared A_{112}[b] (C_6H_{12}[e]) 2020cm^{-1}	Ultraviolet $\bar{A}_{DU}$[c] (C_6H_{12}[e]) 2910Å	Ultraviolet $\bar{A}_{C}$[d] (C_6H_{12}[e]) 2910Å
	10/18	1.94		0.363		1.28				
	10/18	1.92						0.366		0.974
	10/18	1.87						0.347		1.002
2-N	11/16	2.40		0.336						
	11/16	0.960[g]			1.200					
	11/16	2.47[h]		0.368						
	11/16	2.47[i]		0.366						
	11/16	0.734[j]			1.218					
	11/16	0.986[k]			1.217					

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[g] Obtained by dilution.

[h] Obtained by dilution of a common sample.

[i] Obtained by dilution of a common sample.

[j] Obtained by dilution of third analysis on 11/16.

[k] Obtained by dilution of fourth analysis on 11/16.

Table 1. (Continued)

Fraction	Date	Bulk conc. (gm/l)	Infrared		Ultraviolet		Infrared		Ultraviolet	
			$\bar{A}_{13}$[a] (CCl_4) 2020cm^{-1}	$\bar{A}_{112}$[b] (CCl_4) 2020cm^{-1}	$\bar{A}_{DU}$[c] (CCl_4) 2850Å	$\bar{A}_{C}$[d] (CCl_4) 2850Å	$\bar{A}_{13}$[a] (C_6H_{12}[e]) 2020cm^{-1}	A_{112}[b] (C_6H_{12}[e]) 2020cm^{-1}	$\bar{A}_{DU}$[c] (C_6H_{12}[e]) 2910Å	$\bar{A}_{C}$[d] (C_6H_{12}[e]) 2910Å
	11/16	2.13						0.379		0.948
	11/16	2.08						0.386		0.934
	1/27	2.99					0.313	0.392		0.941
	1/27	2.64					0.308	0.397		0.959
	1/27	1.91	0.338	0.368	1.223	1.201				
	1/27	1.99	0.327	0.360	1.224	1.213				

quantitative, molar extinction coefficients were calculated from the January 27 data and are listed in Table 2.

If the molar extinction coefficients are used to calculate purities of the various RR' fractions listed in Table 2, the purities of the different fractions as calculated from the ultraviolet extinction coefficient are clustered around 89 per cent RR'. On the other hand, the same calculation

Table 2. Infrared and ultraviolet, molar extinction coefficients for dimethyl-N-(2-cyano-2-propyl)-ketenimine in carbon tetrachloride and cyclohexane

Solvent	Ultraviolet molar extinction coefficient Cary Model 12[a] l.moles^{-1}cm.$^{-1}$	Infrared molar extinction coefficient P.E. 13[b] l.moles^{-1}cm.$^{-1}$	Infrared molar extinction coefficient P.E. 112[c] l.moles^{-1}cm.$^{-1}$
CCl_4[d]	191[c]	553[e]	604[e]
C_6H_{12}[f]	149.5[g]	514[e]	645[e]

[a] Results with the Beckman Model DU are in exact agreement with those obtained with the Cary Model 12.

[b] Perkin-Elmer Model 13.

[c] Perkin-Elmer Model 112.

[d] Measured at 2850Å.

[e] Measured at 2020 cm.$^{-1}$.

[f] Cyclohexane.

[g] Measured at 2900Å.

gives quite a wide range of values (some over 100 per cent) when the infrared extinction coefficients are used. On this basis, all calculations of the purity of relatively pure RR' samples have been made using the ultraviolet method of analysis.

The ultraviolet absorption spectrum of RR' in cyclohexane is symmetrical about 2900Å. In contrast to this, the ultraviolet spectrum of RR' in carbon tetrachloride has a "shoulder" with the nearly horizontal point of inflection centered at 2850Å. The use of specially purified carbon tetrachloride, which should certainly have been free of any traces of carbon disulfide, had no effect on this shoulder. Small amounts of carbon tetrachloride added to a solution of RR' in cyclohexane had no effect on the spectrum. Therefore, it is thought that the effect is due directly to the solvent.

RR' in the presence of air turns yellowish quite rapidly. Although the extent of this reaction is small at room temperature, these yellow products do seriously interfere with the determination of RR' by the ultraviolet method as they absorb around the region of 2900Å. However, their presence is indicated by the fact that they destroy the symmetry of the RR' peak in cyclohexane. Since the shape of the peak as well as the peak height was important in interpreting the ultraviolet data, the Cary Model 12, which is a recording instrument, was used more often than the Beckman Model DU in analyses.

RESULTS

Dilatometric Studies

General treatment of data

The cathetometer readings obtained in each run were plotted as a function of time. These readings record directly the changes in height of the solution meniscus in the capillaries of the dilatometer and are related by Equation 19 to the change of density of the solution. Since Goldfinger and Lauterbach[109] have reported the relationship (which is linear up to 1.5 mole per cent) between mole per cent conversion of styrene to polystyrene and the density of the solution at the temperature of these experiments, the measurement of the slope of the above plots together with the calibration of the dilatometer permit one to calculate the rate of polymerization by Equation 21. The value of the constant, $\frac{M}{100}\frac{dX}{dD}D$, in Equation 21 is 48.19 moles $1.^{-1}$ at 70°. It was assumed not to change in styrene solutions of benzene. Since benzene and styrene form an ideal solution[110], this assumption seems reasonable. Schulz and Harborth[111] have in fact shown that

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[109] G. Goldfinger and K. Lauterbach, *J. Polymer Sci.*, **3**, 145 (1948).

[110] R. H. Boundy and R. F. Boyer, "Styrene, Its Polymers, Copolymers and Derivatives", p. 65, Reinhold Publishing Corp., New York, N. Y. (1952).

[111] G. V. Schulz and G. Harborth, *Angew. Chem.*, **59**, 90 (1947).

the solution density of polystyrene in benzene and styrene is the same.

$$(1) \quad dD = \frac{2AD}{V} dh$$

$$(2) \quad R_p = \frac{M}{100} \frac{dX}{dD} \frac{dD}{dt}$$

$$(3) \quad R_p = \frac{M}{100} \frac{dX}{dD} \frac{2AD}{V} \frac{dh}{dt}$$

in which D = density of the solution.
A = area of one capillary.
V = volume of volume cell.
h = cathetometer reading.
R_p = rate of polymerization.
M = molarity of pure monomer.
X = mole per cent monomer converted to polymer.
t = time.

Table 3 shows the results of the calibration of the various dilatometers used in this investigation. The volume of the volume cell, the capillary diameter, and the approximate diameter and height of the volume cell are tabulated. The volume tabulated is a hypothetical volume calculated to be the volume of the dilatometer volume cell if the capil-

Table 3. Calibration constants for dilatometers

Dilatometer designation	Volume[a] of dilatometer volume cell ml.	Capillary diameter mm.	Height[b] of volume cell mm.	Diameter[b] of volume cell mm.
NTBC	19.005	1.27	46.0	31.0
NTBCL	17.906	1.18	74.8	22.7
V, VI[c]	17.317	1.01	64.8	22.6
NTB[d]	23.993	1.26	-	-
I, II[c]	19.959	1.02	47.0	30.0
III, IV[c]	22.70	(1.01)[e]	50.5	30.0
TB-4[c]	17.69	(1.01)[e]	68.8	22.3

[a] A hypothetical volume calculated from calibration data assuming dilatometer capillary extended uniformly to "zero" point[112] on the dilatometer.

[b] Approximate dimensions of the volume cell of the dilatometers.

[c] Dilatometers constructed from precision bore tubing.

[d] This dilatometer was broken in the course of the investigation and while the values for the length and width were not recorded, they were similar in ratio to dilatometer NTBC.

[e] Values assumed from manufacturers specifications of the precision bore capillary tubing.

laries extended uniformly to the "zero" point[112] of the dilatometer. A volume correction, calculated by multiplying the total capillary area by the distance which the meniscus reading was below the "zero" point, was subtracted from the tabulated hypothetical volume to give a volume which was used in the calculation of the rates of polymerization by Equation 21.

A typical plot of dilatometer readings as a function of time is shown in Figure 1 for the azo-bis-isobutyronitrile (ABN) initiated polymerization of styrene with 2,6-dichloroquinone, a strong inhibitor, present. The nearly horizontal portion of the curve defines the inhibition period. After the inhibitor is consumed, the rate usually (depending on the chemical nature of the inhibition products) increases to the uninhibited rate. The time during which the inhibitor is consumed is termed the inhibition (or induction) period and is determined graphically by the intersection of a line drawn through the points recorded during the inhibition period and a line drawn immediately after the rate has increased to its uninhibited value. Two such lines have been constructed in

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[112] The "zero" point was a unique and visually distinctive position arbitrarily chosen on each dilatometer. Quite often it would correspond to the top of one of the capillaries. Its purpose was two-fold. Firstly, periodic checking of the "zero" point during the run assured one that the dilatometer (or cathetometer) had not been moved. Secondly, it permitted the use of an appropriate value for the volume in the calculation of the rate of polymerization as described in the text.

Figure 1. A typical initiated styrene polymerization with inhibitor present

Ordinate: dilatometer readings in cm.
Abscissa: time in hours.

Run 55

$(\text{Styrene})_o = 2.44$ moles $l.^{-1}$.

$(\text{Azo-}\underline{\text{bis}}\text{-isobutyronitrile})_o = 0.01075$ moles $l.^{-1}$.

$(\text{2,6-Dichloroquinone})_o = 0.00315$ moles $l.^{-1}$.
Temperature = 70.0°
Dilatometer V, VI

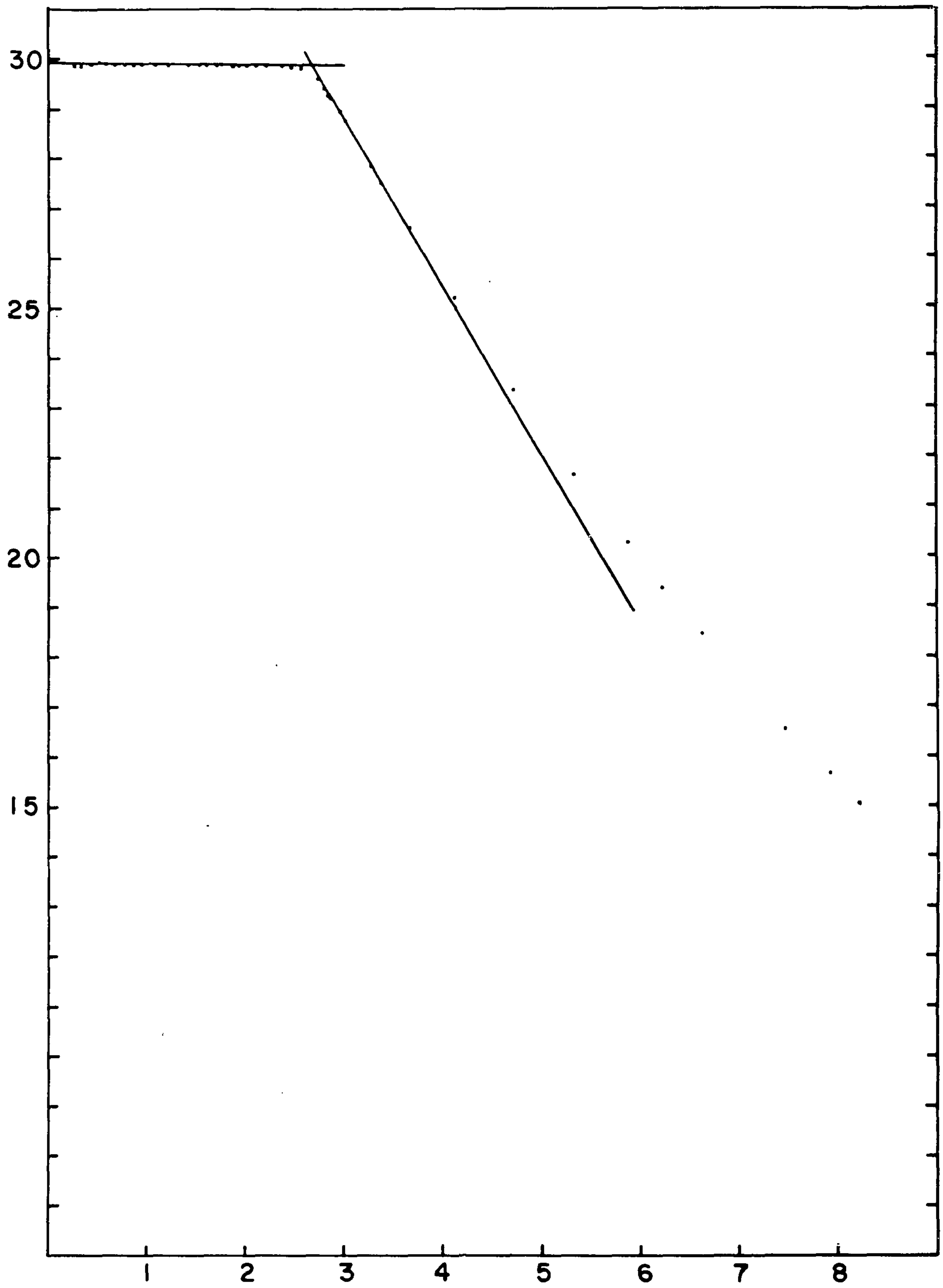
30
25
20
15
1
2
3
4
5
6
7
8

Figure 1 and they intersect at 2.68 hours[113]. In the case of a strong inhibitor, this procedure permits a precise value to be assigned to the inhibition period. For a weaker inhibitor the above procedure can become subjective, and Burnett and Cowley[114] have presented a method for objective assignment of inhibition periods based on a mathematical analysis of the kinetics of inhibition. With the exception of diphenylpicrylhydrazyl (DPPH), all of the inhibitors used in this investigation were inhibitors with no complications resulting from retardation of rate after the end of the inhibition periods. DPPH does not fit simply into the above scheme[114], as was noted by Burnett and Cowley, and the treatment of these curves will be presented later in this subsection together with the results.

The polymerization in the absence of inhibitor with similar concentrations of monomer and initiator would, at the same temperature, give a curve like that shown in Figure 1 after the end of the inhibition period. Rates of polymerization were calculated using Equation 21 for all runs in which calibrated dilatometers were used. Although no quantitative

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[113] In this case (Run 55) the period is 2.65 hours since the "zero" inhibition time corresponded to 0.03 hour rather than 0.00 hour.

[114] G. M. Burnett and P. R. E. J. Cowley, Trans. Faraday Soc., 49, 1490 (1953).

discussion of the rates before and after the inhibition period is given in this thesis, the values calculated are given for the inhibited runs. In the uninhibited runs in which the purpose of the run was to determine the rate of polymerization, much larger plots of the data were made than the one shown in Figure 1 and slopes were determined using a 4 inch by 6 inch first-surface aluminized, optical flat.

One other feature of the data may be noted in Figure 1 by observing that the rate of polymerization slowly decreases during the run. This effect is particularly evidenced by the points which drift away from the line constructed from the uninhibited rate immediately following the inhibition period. The decrease in rate is undoubtedly due to the fact that appreciable amounts of initiator are decomposed during a run at 70°. In some runs, a second slope has been determined at a later time to show the magnitude of the effect. In Run 42 enough data were obtained so that the rate constant for the decomposition of dimethyl-N-(2-cyano-2-propyl)-ketenimine (RR') in styrene could be estimated from the decrease in rate of polymerization as a function of time. The treatment of these data is presented later in this subsection.

All inhibition periods were treated as if the inhibitor simply counted the rate of initiation by terminating growing chains with a definite stoichiometry. The rate of initiation, R_i, is given by Equation 22 in which k is the rate of decomposition of initiator, (I) is the initiator concentration, and a is the initiator efficiency. During the inhibition period, the rate of termination is equal to q times the rate of disappearance of inhibitor, $\frac{d(In)}{dt}$. The factor q is the inhibitor stoichiometry which is defined as the number of radicals, R•, which react with an inhibitor molecule to give inactive products, Equation 5. Setting the rate of initiation of radicals equal to the rate of their termination, one obtains Equation 6. Substitution of the exponential dependence of the initiator on time and integrating over the length of the induction period, T, Equation 7 is obtained. The ratio, a/q, was tabulated for each inhibition period observed using the value of k for the monomer concentration at which the run was made.

(4) $R_i = 2ak(I)$

(5) $qR\cdot + In \longrightarrow$ Inactive products

(6) $- \frac{d(In)}{dt} = 2ak(I)$

(7) $q(In)_o = 2a(I)_o(1 - e^{-kT})$

In addition, where more than one concentration of inhibitor was used at the same monomer and initiator concentration, the effects of the initial 12 to 15 minutes of warm up required for the solution to approach thermal equilibrium may be minimized by subtraction to give Equation 8 where the subscripts 1 and 2 refer to the different amounts of inhibitor in the two runs considered. Values of <u>a</u>/<u>q</u> have been calculated in this manner when possible.

$$(8)\quad q(In)_{o2} - q(In)_{o1} = 2a(I)_o(e^{-kT_1} - e^{-kT_2})$$

As was indicated in the Historical Section, such a simple view of the mechanism of inhibition is unrealistic in view of the complexities of the inhibition process. However, it does represent a convenient system for comparing the data with the different inhibitors and initiators.

All concentrations unless otherwise noted are given for the temperature at which the run was made. These concentrations were calculated from the concentrations at room temperature by multiplying the room temperature concentration by the ratio of the density of the solution at the temperature of the run to the density of the solution at room temperature. The density of styrene for different temperatures was obtained by interpolation of data given in Boundy and Boyer[115]. The density of benzene for different temperatures was calculated from data given in the "International Critical Tables"[116]. The densities of solutions of styrene and benzene were calculated assuming that the specific volume of the solution was a linear function of the weight fraction of either component.

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[115] R. H. Boundy and R. F. Boyer, <u>op. cit</u>., p. 55.

[116] "International Critical Tables", Vol. III, p. 27, McGraw-Hill Book Co., Inc., New York, N. Y. (1928).

Rate of polymerization of styrene as a function of initiator concentration

The rates of polymerization in pure styrene at 70.0° are given in Table 4 for seven runs in which the concentration of RR' has been varied over a fifty-fold range. Two of the runs, Run 14 and Run 19, have been reported by Trapp[117] and are included here for comparison. Also, two runs of ABN-initiated polymerization of pure styrene at 70.0° are included in the table.

In Figure 2, the square of the rate of polymerization plotted against initiator concentration for RR' gives a linear plot within experimental error. Actually the points for Runs 14 and 19 (triangles on plot) agree better than they should as Trapp's[117] data were used directly for this calculation and as is explained in footnote c of Table 4, for comparison with the method of calculating rates in this thesis, the values of the rates of polymerization should be somewhat lower.

If the rate of thermal initiation were appreciable, Tobolsky[118] has shown that, assuming termination is bimolecular in free radicals, the above plot would not be linear unless the square of the rate of thermal polymerization were

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[117] O. D. Trapp, Unpublished Ph.D. Thesis, p. 90, Iowa State College Library, Ames, Iowa (1957).

[118] A. V. Tobolsky, Ann. Rev. Phys. Chem., 7, 170 (1956).

Figure 2. Square of rate of polymerization of styrene at 70.0° as a function of dimethyl-N-(2-cyano-2-propyl)-ketenimine concentration

Ordinate: rate of polymerization squared x 10^4 moles l.$^{-1}$ sec.$^{-1}$

Abscissa: molarity of dimethyl-N-(2-cyano-2-propyl)-ketenimine

—○— points determined in this investigation

—▽— points reported by Trapp[117]

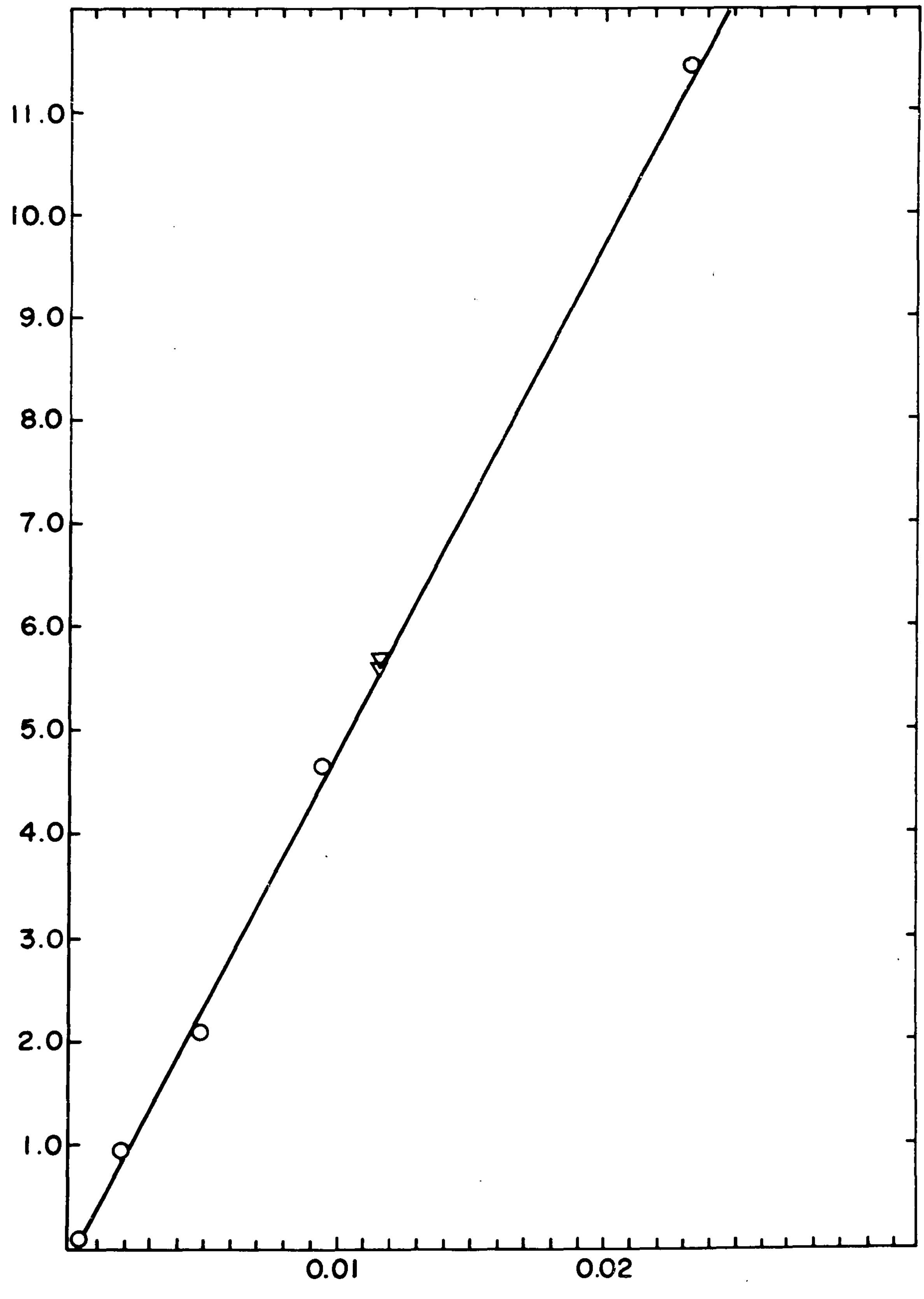
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.01
0.02

Table 4. Rate of polymerization of pure styrene at 70.0° initiated by dimethyl-N-(2-cyano-2-propyl)-ketenimine and azo-<u>bis</u>-isobutyronitrile

Run	Dilatometer designation	Initiator	Initial initiator molarity $\times 10^2$	$R_p \times 10^4$ moles l.$^{-1}$ sec.$^{-1}$	$(R_p)^2 \times 10^8$ moles^2 l.$^{-2}$ sec.$^{-2}$	$(R_p)^2-(R_{p_{Th}})^2 \times 10^8$ [a]	$\frac{R_p^2}{k(I)(M)^2} \times 10^3$ l.mole^{-1}sec.$^{-1}$
33	NTBCL	RR'[b]	2.34	3.38	11.42	11.42	1.156
14[c]	I, II	RR'	1.167[c]	2.29[c]	5.24	5.24	1.064
19[c]	I, II	RR'	1.161[c]	2.24[c]	5.02	5.02	1.024
41	NTBC	RR'	0.948	2.17	4.71	4.71	1.177
32	V, VI	RR'	0.484	1.44	2.07	2.07	1.007
34	III, IV	RR'	0.198	0.964	0.929	0.926	1.112

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[a] $R_{p_{Th}}$ = rate of thermal polymerization = 0.055×10^{-4} mole l.$^{-1}$sec.$^{-1}$ at 70.0°.

[b] RR' = dimethyl-N-(2-cyano-2-propyl)-ketenimine.

[c] Run 14 and run 19 were reported by Trapp[117] as Runs 86K and 94K respectively. RR' was weighed and its purity was estimated by Dr. O. D. Trapp. The rates of polymerization, R_p are slightly lower than those measured by Trapp as he measured the rate of polymerization between 15 and 20 minutes after the run had started. In this table the rate was computed using data between 20 and 30 minutes and is consequently lower. Also, there exists a small difference in the value used to convert per cent contraction to per cent monomer conversion which operates in the same direction.

Table 4. (Continued)

Run	Dilatometer designation	Initiator	Initial initiator molarity x 10^2	R_p x 10^4 moles $l.^{-1}$ $sec.^{-1}$	$(R_p)^2$ x 10^8 $moles^2$ $l.^{-2}$ $sec.^{-2}$	$(R_p)^2$-$(R_{p_{Th}})^2$ x 10^8	$\frac{R_p^2}{k(I)(M)^2}$ x10^3 l. $mole^{-1}$ $sec.^{-1}$
42	I, II	RR.'	0.0415	0.319	0.102	0.099	0.580
20	NTB	ABN[d]	1.000	2.121	4.50	4.50	1.439
43	NTBCL	ABN	0.0356	0.445	0.198	0.195	1.784

[d] ABN = azo-bis-isobutyronitrile.

subtracted from it. In Table 4 it may be seen that such a correction is negligible for these data.

Rate of initiated polymerization of styrene as a function of monomer concentration

The rate of polymerization of styrene initiated both by ABN and RR' are tabulated at different monomer concentrations in Table 5. The next to last column of Table 5 shows that the data do not fit Equation 9. These data will be considered in the Discussion Section of this thesis.

$$(9) \qquad R_p = k_p \frac{a^{\frac{1}{2}} k^{\frac{1}{2}} (I)^{\frac{1}{2}}}{k_t^{\frac{1}{2}}} (M)$$

in which R_p = the rate of polymerization

k_p = the chain propagation constant

a = the initiator efficiency factor

k = the first order rate of decomposition for initiator

M = the monomer concentration.

Azo-bis-isobutyronitrile-initiated polymerization of styrene at 70.0° inhibited by chloranil, 2,5-dichloroquinone, 2,6-dichloroquinone, and diphenylpicrylhydrazyl

Table 6 presents the results of the inhibition of the ABN-initiated polymerization of styrene at 70.0°. The induc-

Table 5. Rate of polymerization of styrene solutions in benzene at 70.0° initiated by dimethyl-N-(2-cyano-2-propyl)-ketenimine and azo-bis-isobutyronitrile

Run	Dilatometer designation	Initiator	Initial initiator molarity x 10^2	Styrene molarity	$R_p \times 10^4$ moles l.$^{-1}$ sec.$^{-1}$	$\frac{R_p^2}{k(I)(M)^2} \times 10^3$ l. mole^{-1} sec.$^{-1}$	$k \times 10^5$ [a] sec.$^{-1}$
20	NTB	ABN[b]	1.000	8.28	2.121	1.439	4.56
63	V, VI	ABN	1.073	2.44	0.496	0.887	(4.34)
64	I, II	ABN	1.073	0.816	0.1308	0.559	(4.28)
34	III, IV	RR'[c]	0.198	8.28	0.964	1.112	6.15
65	III, IV	RR'	0.744	2.44	0.475	0.963	5.28
66	TB-4	RR'	1.044	0.816	0.129	0.544	(4.40)

[a] First order rate constant for decomposition of initiator as determined in this investigation. Values in parentheses correspond to interpolated values.

[b] ABN = azo-bis-isobutyronitrile.

[c] RR' = dimethyl-N-(2-cyano-2-propyl)-ketenimine.

Table 6. The inhibition of azo-*bis*-isobutyronitrile initiated styrene polymerization at 70.0° by chloranil, 2,5-dichloroquinone, 2,6-dichloroquinone, and diphenylpicrylhydrazyl

Run	Dilatometer designation	Styrene molarity	Initial initiator molarity x 10^2	Inhibitor	Initial inhibitor molarity x 10^2	Inhibition period, hours	*a*/*q* [a]
5	NTBCL	8.28[b]	0.976	chloranil	0.301	0.67	1.49
6	NTB	8.28[b]	1.000	chloranil	0.632	1.13	1.87
59	I, II	8.28[b]	1.089	chloranil	0.934	1.40	2.08
16	NTB	4.10	0.785	chloranil	0.224	1.36	0.735
J21[c]	I[d]	4.07	0.785	chloranil	0.437	2.37	0.892
17	NTBC	4.10	0.785	chloranil	0.630	3.52[e]	0.939

[a] The value of 4.25 x 10^{-5}, 4.40 x 10^{-5}, and 4.56 x 10^{-5} were used as the value for the rate of decomposition of azo-*bis*-isobutyronitrile for styrene molarities of 2.44, 4.10, and 8.28, respectively.

[b] Molarity of undiluted monomer at 70.0°.

[c] Run made on June 21, 1956 using Tanaka's vacuum system (see Apparatus Subsection of Experimental Section) for degassing the solutions. Dilatometer volume cell was only part of dilatometer immersed in constant temperature bath, temperature 70.2°.

[d] An uncalibrated dilatometer.

[e] Glass enclosed nail stirrer broke during degassing. Stirrer was enclosed in glass *in vacuo* so effect of oxygen is probably negligible for an initiated run.

Table 6. (Continued)

Run	Dilatometer designation	Styrene molarity	Initial initiator molarity x 10^2	Inhibitor	Initial inhibitor molarity x 10^2	Inhibition period, hours	a/q
10	NTBC	2.44	0.935	chloranil	0.322	2.25	0.590
11	NTB	2.44	0.963	chloranil	0.605	4.83[e]	0.602
51	NTBC	8.28[b]	1.089	2,5-dichloroquinone	0.956	3.40	1.023
49	III, IV	2.44	1.076	2,5-dichloroquinone	0.949	6.67	0.688
56	III, IV	8.28[b]	1.089	2,6-dichloroquinone	0.319	1.42	0.703
55	V, VI	2.44	1.075	2,6-dichloroquinone	0.315	2.65	0.439
68	UCTB-6[f]	8.28[b]	1.017	DPPH[g]	0.563	2.20[h]	0.914

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[f] Uncalibrated dilatometer constructed with precision bore tubing.

[g] DPPH = diphenylpicrylhydrazyl.

[h] Inhibition periods not clearly defined dilatometrically (cf. Figure 3) so the disappearance as observed visually of the purple color characteristic of DPPH was taken represent the best estimate of the length of the induction period and is tabulated here.

Table 6. (Continued)

Run	Dilatometer designation	Styrene molarity	Initial initiator molarity x 10^2	Inhibitor	Initial inhibitor molarity x 10^2	Inhibition period, hours	*a*/*q*
75	III, IV	4.10	1.004	DPPH[g, i]	0.335	1.77[h]	0.683
67	UCTB-5[f]	2.44	0.995	DPPH[g]	0.554	2.52[h]	0.875

[i] DPPH from fresh preparation in contrast to DPPH used in Runs 68 and 67 (two years old).

tion period, the calculated quantity, a/q (initiator efficiency divided by inhibitor stoichiometry assuming simple mechanism of inhibition as presented earlier in this subsection), are tabulated in this table. The assignment of the induction periods was done by using the dilatometric data in all cases except Runs 67, 68, and 75 with DPPH. These runs with DPPH are plotted in Figure 3. Induction periods have been estimated graphically (in the manner discussed earlier). The values of 2.83 and 1.83 hours for Runs 68 and 75 respectively, were obtained, but the construction in this case seems somewhat subjective. Moreover, with Run 67, the data do not permit an analysis by this method. Fortunately the time at which the violet color of DPPH disappeared was recorded in these runs. It should be noted that while the disappearance of this color took place over a period of roughly three to ten minutes[119], its disappearance could be assigned objectively in each run. The values for the time at which the last DPPH color left the volume cell are given as the inhibition periods in Table 6.

Table 7 contains values of a/q calculated using Equation 8, p. 89. Effects of temperature equilibration at the beginning of a run are minimized by subtracting the number of radicals

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[119] Eight minutes, three minutes, and seven minutes in Runs 67, 68, and 75 respectively.

Figure 3. Inhibition of azo-*bis*-isobutyronitrile initiated polymerization of styrene at 70.0° by diphenylpicrylhydrazyl

Ordinate: cathetometer readings in cm.
Abscissa: time in hours

Bottom curve[a] - Run 67 (Table 6)
Middle curve[a] - Run 75 (Table 6)
Lower curve[a] - Run 68 (Table 6)

---

[a] At left hand margin.

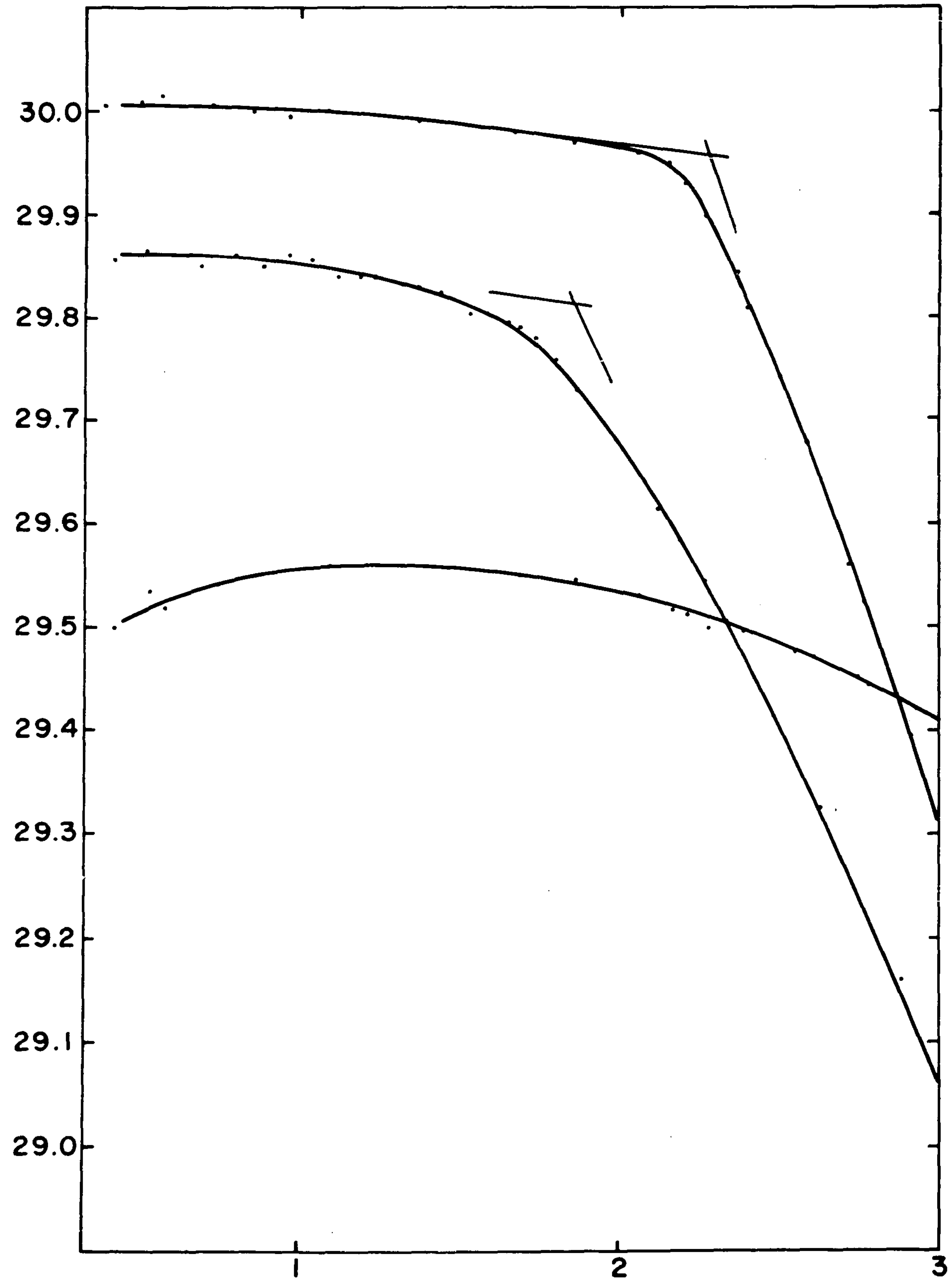
30.0
29.9
29.8
29.7
29.6
29.5
29.4
29.3
29.2
29.1
29.0
1
2
3

Table 7. Chloranil inhibition data of azo-bis-isobutyronitrile-initiated styrene polymerization at 70.0° corrected for initial temperature equilibration of dilatometers

Runs subtracted	Styrene molarity	a/q [a]
5 - 6	8.28[b]	2.48
6 - 59	8.28[b]	3.94
5 - 59	8.28[b]	2.99
16 - J21	4.10	1.15
J21- 17	4.10	1.06
16 - 17	4.10	1.11
10 - 11	2.44	0.65

[a] This quantity was calculated according to Equation 8, p. 89, and the values of 4.25×10^{-5}, 4.40×10^{-5}, and 4.56×10^{-5} were used as the values for the rate of decomposition of azo-bis-isobutyronitrile for styrene molarities of 2.44, 4.10, and 8.28 respectively.

[b] Molarity of undiluted monomer at 70.0°.

counted by an inhibitor in one run from the number counted in a second run at higher inhibitor concentration (initiator and monomer concentration remain constant). While the runs subtracted in compiling Table 7 are not all strictly comparable in this manner as may be seen by inspection of Table 6, it is clear that elimination of transient effects at the start of the run serves only to enhance the variation of a/q with monomer concentration.

The rates of the ABN-initiated polymerization at 70.0° before and after the inhibition period are tabulated in Tables 8, 9, and 10. Each table covers a different monomer concentration. DPPH solutions in styrene are not stable at room temperature in the presence of oxygen. Although this effect has been reported in the literature[120, 121], its magnitude was not realized at first in this investigation. In the runs in which DPPH was not weighed separately into its own reservoir (in order to prevent DPPH from coming into contact with oxygen and styrene simultaneously), no inhibition period was observed. In fact, in some of these runs the purple color characteristic of DPPH was completely exhausted before the runs were degassed (in less than one hour, standing at room temperature). These "oxygenated" DPPH runs serve no purpose as far as the estimation of initiator efficiency is concerned. However, they do give a comparison of the rate of polymerization after the DPPH has been consumed with other post-inhibition polymerization rates.

The following mechanism of inhibition, Equations 10 to 15, was examined for the ABN-initiated experiments with chloranil, in which I is initiator, R· is a radical derived

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[120] A. Chapiro, J. Durup, and J. Grosmangin, J. chim. phys., 50, 482 (1953).

[121] K. E. Russell and A. V. Tobolsky, J. Am. Chem. Soc., 75, 5052 (1953).

Table 8. Rates of azo-bis-isobutyronitrile-initiated polymerization of pure styrene at 70.0° during and after inhibition period with chloranil, 2,5-dichloroquinone, 2,6-dichloroquinone, and diphenylpicrylhydrazyl

Run	Initial initiator molarity x 10^2	Inhibitor	Initial inhibitor molarity x 10^2	Time after start of run, hours	R_p x 10^4 moles $l.^{-1}$ $sec.^{-1}$
5	0.976	chloranil	0.301	0.92	2.013
6	1.000	chloranil	0.632	0.67 1.33	0.0932[a] 2.18
59	1.089	chloranil	0.934	1.00 1.83	0.0912[a] 2.006
51	1.089	2,5-dichloroquinone	0.956	2.00 3.9	0.0300[a] 1.66
56	1.089	2,6-dichloroquinone	0.319	0.67 1.67	0.0212[a] 1.43
58	1.089	DPPH[b]	0.305[c]	1.00 3.00	0.300 0.915

[a] Rate of polymerization during inhibition period.

[b] DPPH = diphenylpicrylhydrazyl.

[c] DPPH essentially destroyed due to oxygen induced reaction in styrene which occurred before degassing.

from the decomposition of initiator, M is monomer, M• is a radical derived by addition of any radical to monomer, In is inhibitor, and In• is a radical derived from inhibitor.

(10) $I \xrightarrow{k} 2R\cdot$ Ri

(11) $R\cdot + M \xrightarrow{k_a} M\cdot$

Table 9. Rates of azo-bis-isobutyronitrile-initiated polymerization of styrene solution (around 4.33 M) during and after inhibition period with chloranil and diphenylpicrylhydrazyl

Run	Initial initiator molarity x 10^2	Inhibitor	Initial inhibitor molarity x 10^2	Time after start of run, hours	R_p x 10^4 moles $l.^{-1}$ $sec.^{-1}$
16^a	0.785	chloranil	0.224	2.00	0.722
				3.75	0.564
$17^{a,b}$	0.785	chloranil	0.630	2.00	0.0310^c
				4.50	0.598
				5.75	0.501
75^d	1.004	DPPH^e	0.335	1.00	0.0057^c
				2.50	0.0531

[a] Styrene molarity = 4.10 moles $l.^{-1}$.

[b] Stirrer broken during degassing.

[c] Rate of polymerization measured during inhibition period.

[d] Styrene molarity = 4.33 moles $l.^{-1}$.

[e] DPPH = diphenylpicrylhydrazyl.

(12) $M\cdot + M \xrightarrow{k_p} M\cdot$ $\qquad k_p(M)(M\cdot)$

(13) $M\cdot + In \xrightarrow{k_{In}} In\cdot$ $\qquad k_{In}(In)(M\cdot)$

(14) $In\cdot + M \xrightarrow{k_{Cop}} M\cdot$ $\qquad k_{Cop}(M)(In\cdot)$

(15) $2In\cdot \xrightarrow{k_t}$ inactive products $\qquad k_t(In\cdot)^2$

The rate of consumption of inhibitor is given by Equation 16 if no inhibitor is regenerated in the termination step.

Table 10. Rates of azo-*bis*-isobutyronitrile-initiated polymerization of styrene solution (2.44 M) during and after inhibition period with chloranil, 2,5-dichloroquinone, 2,6-dichloroquinone and diphenylpicrylhydrazyl

Run	Initial initiator molarity x 10^2	Inhibitor	Initial inhibitor molarity x 10^2	Time after start of run, hours	R_p x 10^4 moles $l.^{-1}$ $sec.^{-1}$
10	0.935	chloranil	0.322	1.50	0.0179[a]
				4.50	0.346
				10.50	0.187
11[b]	0.963	chloranil	0.605	2.50	0.00805[a]
				6.50	0.324
49	1.076	2,5-dichloroquinone	0.949	7.5	0.286
50	1.076	2,5-dichloroquinone	0.949	9.0	0.0042[a]
55	1.075	2,6-dichloroquinone	0.315	1.5	0.0047[a]
				3.15	0.417
48	0.995	DPPH[c]	0.220[d]	3.75	0.269
57	1.075	DPPH[c]	0.301[d]	1.25	0.0491
				6.00	0.217
62	1.075	DPPH[c]	0.546[d]	1.75	0.231
				8.00	0.770

---

[a] Rate of polymerization during inhibition period.

[b] Stirrer broken during degassing.

[c] DPPH = diphenylpicrylhydrazyl.

[d] DPPH essentially destroyed due to oxygen-induced reaction in styrene which occurred before degassing.

The steady state approximation applied to all radicals in solution gives Equation 17 and when applied to the species M•, it gives Equation 18. Elimination of (M•) and (In•) from these equations gives Equation 19.

$$(16)\quad -\frac{d(\mathrm{In})}{dt} = k_{\mathrm{In}}(\mathrm{In})(\mathrm{M}\cdot)$$

$$(17)\quad R_i = 2k_t(\mathrm{In}\cdot)^2$$

$$(18)\quad \frac{d(\mathrm{M}\cdot)}{dt} = 0 = R_i - k_{\mathrm{In}}(\mathrm{In})(\mathrm{M}\cdot) + k_{\mathrm{Cop}}(\mathrm{In}\cdot)(\mathrm{M})$$

$$(19)\quad -\frac{d(\mathrm{In})}{dt} = R_i + k_{\mathrm{Cop}}\frac{R_i^{\frac{1}{2}}}{(2k_t)^{\frac{1}{2}}}(\mathrm{M})$$

Since the rate of initiation may in general be written as Equation 20, in which a is the initiator efficiency, Equation 19 may be integrated over an inhibition period T to give Equation 21, in which the subscript zero on a concentration denotes an initial concentration.

$$(20)\quad (\mathrm{I}) = (\mathrm{I})_o\, e^{-kT}$$

$$(21)\quad (\mathrm{In})_o = 2a(\mathrm{I})_o(1-e^{-kT}) + \frac{2k_{\mathrm{Cop}}}{k_t^{\frac{1}{2}}}a^{\frac{1}{2}}(\mathrm{I})_o^{\frac{1}{2}}(\mathrm{M})_o(1-e^{-\frac{kT}{2}})$$

An attempt was made to fit the chloranil data from the ABN-initiated polymerization to Equation 21. Let Z_1 be defined as equal to $\frac{2(\mathrm{I})_o}{(\mathrm{In})_o}(1 - e^{-kT})$ and let Z_2 be defined as equal to $\frac{(I)_o^{\frac{1}{2}}}{(In)_o}(1 - e^{\frac{-kT}{2}})$. If the initiator efficiency is a constant independent of monomer concentration, a plot of Z_1 versus Z_2 should, for points of a common monomer concentration, define a straight line whose slope is proportional to the first power of the monomer concentration. Z_1 and Z_2 are tabulated in Table 11 as well as slopes constructed from a plot of Z_1 versus Z_2 (not shown). These slopes are certainly not such a simple function of monomer concentration as the above equation would suggest. Also in Table 11 there are tabulated values of aZ_1 and $a^{\frac{1}{2}}Z_2$. These values have been calculated assuming relative values of $\underline{a}$ calculated from the rates of polymerization. The assumed $\underline{a}$ values are also tabulated. Slopes (which were obtained as in the case of Z_1 and Z_2) of points at common monomer concentration are given and again fit no better than the previous treatment. The time that is required to establish thermal equilibrium at the start of a run may be enough to vitiate this treatment. Also it should be noted that in this treatment no account has been taken of initiation by RR' formed from ABN during the inhibition period.

Dimethyl-N-(2-cyano-2-propyl)-ketenimine-initiated polymerization of styrene at 70.0° inhibited by chloranil

Table 12 presents the results of the inhibition of RR' initiated polymerization of a styrene at 70.0° by chloranil.

Table 11. Inhibitor data calculated according to the copolymerization equation

Run	Monomer molarity	Z_1[a]	Z_2[b] $l.^{\frac{1}{2}}$ $moles^{-\frac{1}{2}}$	Slope[c] of points of common monomer molarity	a	aZ_1[a]	$a^{\frac{1}{2}}Z_2$[b] $l.^{\frac{1}{2}}$ $moles^{-\frac{1}{2}}$	Slope[d] of points of common monomer molarity
5	8.28	0.672	1.741	0.355	1.00	0.672	1.741	0.386
6	8.28	0.534	1.401		1.00	0.534	1.401	
59	8.28	0.479	1.117		1.00	0.479	1.117	
16	4.10	1.360	4.05	0.475	0.76	1.030	3.62	0.279
J21	4.07	1.121	3.462		0.76	0.851	3.02	
17	4.10	1.065	3.42		0.76	0.807	2.98	
10	2.44	1.695	4.74	-0.193	0.62	1.285	3.73	-0.875
11	2.44	1.660	4.96		0.62	1.260	3.90	

[a] $$Z_1 = \frac{2(I)_o}{(In)_o}(1 - e^{-kT}) = \frac{q}{a}\ .$$

[b] $$Z_2 = \frac{(I)_o^{\frac{1}{2}}}{(In)_o}(1 - e^{\frac{-kT}{2}}).$$

[c] Determined from a plot of Z_1 versus Z_2.

[d] Determined from a plot of aZ_1 versus $a^{\frac{1}{2}}Z_2$.

Table 12. The inhibition of dimethyl-N-(2-cyano-2-propyl)-ketenimine-initiated styrene polymerization by chloranil

Run	Dilatometer designation	Styrene molarity x 10^2	Initial initiator molarity	Initial chloranil molarity x 10^2	Inhibition period, hours	a/q [a]
52	NTBCL	8.28[b]	1.143	0.364	0.65	1.163
45	NTBC	8.28[b]	1.13	0.634	1.02	1.362
53	V, VI	2.44	1.191	0.358	1.97	0.479
44	III, IV	2.44	1.14	0.624	3.95	0.518

[a] For the calculation of this quantity, the values of 6.27×10^{-5} and 5.30×10^{-5} sec.$^{-1}$ were used as the values of the rate of decomposition of dimethyl-N-(2-cyano-2-propyl)-ketenimine for styrene molarities of 8.28 and 2.44 respectively.

[b] Molarity of undiluted styrene at 70.0°.

Qualitatively, the inhibition periods resembled those from the chloranil inhibition of ABN initiated polymerization of styrene. The induction period and the quantity, $\underline{a}/\underline{q}$ (initiator efficiency divided by inhibitor stoichiometry assuming simple mechanism as presented earlier in this subsection), are tabulated in Table 12. The assignment of induction periods was done from the dilatometric data.

The rates of RR'-initiated styrene polymerization during and after the inhibition period with chloranil are tabulated in Table 13. It should be noted that two different monomer concentrations are reported in this table.

The inhibition of thermally-initiated styrene polymerization

The results of the inhibition of the thermally initiated rate of polymerization of styrene by chloranil are given in Table 14. The inhibition periods as well as the rates of polymerization are given in this table. For comparison, Run 18, in which rate of uninhibited thermal initiation was measured, is included. Two other runs made with DPPH in 4.33 and 2.44 molar styrene gave color changes after around 60 hours but dilatometric inhibition periods could not be estimated. Russell and Tobolsky[121] have indicated that DPPH is not stable at these temperatures. Its rather rapid disappearance in these longer runs may result from a process other than con-

Table 13. Rates of polymerization of styrene solution at 70.0° initiated by dimethyl-N-(2-cyano-2-propyl)-ketenimine and inhibited by chloranil

Run	Initial monomer molarity	Initial initiator molarity x 10^2	Initial inhibitor molarity x 10^2	Time after start of run, hours	R_p x 10^4 moles $l.^{-1}$ $sec.^{-1}$
52	8.28[a]	1.143	0.364	0.5	0.094[b]
				0.9	2.26
45	8.28[a]	1.13	0.634	0.67	0.0916[b]
				0.45	2.22
53	2.44	1.191	0.358	0.80	0.0400[b]
				2.30	0.451
44	2.44	1.14	0.624	2.25	0.0273[b]
				5.00	0.439

[a] Molarity of undiluted monomer.

[b] Rate of polymerization determined during the inhibition period.

sumption of radicals from thermally initiated styrene polymerization.

If one assumes that the rate of thermal initiation is some kinetic order, n, in monomer concentration (Equation 22), and that the rate of consumption of inhibitor is equal to the rate of thermal initiation (Equation 23), then one obtains Equation 24. According to this equation, a plot of the logarithm of the initial inhibitor concentration divided by the resulting inhibition period versus the logarithm of the

Table 14. Inhibition of the thermal polymerization of styrene by chloranil and diphenylpicrylhydrazyl

Run	Initial monomer molarity	Inhibitor	Initial inhibitor molarity x 10^2	Inhibition period, hours	$R_p \times 10^6$ during inhibition period moles $l.^{-1}$ $sec.^{-1}$	$R_p \times 10^6$ after inhibition period moles $l.^{-1}$ $sec.^{-1}$
18	8.28[a]	none	0.000	none	-	5.52
7	8.28[a]	chloranil	0.316	89.0	-	3.04
8	8.28[a]	chloranil	0.621	149.3	-	3.82[b]
13	4.10	chloranil	0.0196	12.8	0.074	2.35[c]
28	2.44	chloranil	0.0098	17.6[d]	-0.083[e]	0.365

[a] Molarity of undiluted monomer at 70.0°.

[b] Rate decreased (smoothly) to 2.65×10^{-6} moles $l.^{-1}$ $sec.^{-1}$ at 195 hours.

[c] Smooth decrease in rate noted although not followed far enough to definitely assign a rate value.

[d] This value is increased to 18.3 if one assumes inhibition period to be flat.

[e] Gradual expansion occurred during inhibition period. It is perhaps due to depolymerization of small amounts of oxygen copolymer formed at room temperature before solutions were degassed.

Table 14. (Continued)

Run	Initial monomer molarity	Inhibitor	Initial inhibitor molarity x 10^2	Inhibition period, hours	R_p x 10^6 during inhibition period moles $l.^{-1}$ $sec.^{-1}$	R_p x 10^6 after inhibition period moles $l.^{-1}$ $sec.^{-1}$
15	2.44	chloranil	0.0232	82	-0.053[e]	0.071
74	8.28[a]	DPPH[f]	0.338	23.7	0.052	0.311

[f] DPPH = diphenylpicrylhydrazyl.

monomer concentration should give a slope of value n. Such a plot was made for the data in Table 14. The fit of the data to this plot was very poor with the scatter of the five experimental points well outside any effects of thermal equilibration of the dilatometers during the first 15 minutes of a run. The plot is not included in this thesis, however, any of a family of lines which one could draw through the points at different monomer concentrations gave slopes much closer to two than three.

$$R_{i_{Th}} = k_n(M)^n \tag{22}$$

$$R_{i_{Th}} = \frac{d(In)}{dt} \tag{23}$$

$$\frac{(In)_o}{T} = k_n(M)^n \tag{24}$$

in which $R_{i_{Th}}$ = rate of thermal initiation.

k_n = rate constant for thermal initiation.

(M) = monomer concentration.

n = kinetic order of thermal initiation step.

(In) = inhibitor concentration.

$(In)_o$ = initial inhibitor concentration.

t = time.

T = inhibition period.

Temperature effects of unstirred reactions and their effect on dilatometric measurements

The topic of temperature effects upon dilatometric measurements has been discussed in detail by Bengough[122]. This author found, in a study of vinyl acetate at 25° (photosensitized), that a rate of 5.3 per cent per hour gave a temperature rise of 2.7° above the bath temperature at the center of the dilatometer and an average temperature rise of 0.9°. In addition he found that errors in estimating inhibition periods dilatometrically might be around 4 to 5 minutes in a typical inhibition experiment. The latter error is small enough to be neglected in this investigation as the errors introduced by temperature equilibration at the start of the run far outweigh it. The other effect, however, could appreciably affect the results of the determination of absolute rates of initiated polymerization. Also the quantitative infrared measurement of rate constants for the decomposition of initiators precisely in monomer could easily be affected.

In view of Bengough's results, a qualitative experiment was done in a reaction tube. The diameter of a reaction tube, 20 mm., was somewhat smaller than the average diameter of the dilatometer, 25 mm., so the following experiment somewhat

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[122] W. I. Bengough, Trans. Faraday Soc., 53, 1346 (1957).

underestimates the effect. Roughly 5 mg. of ABN in 5 ml. of styrene (corresponding approximately to the amount of initiator used in a run) produced a temperature increase of 2° at the center of the reaction tube. It is thus estimated that the average temperature rise was about 1°.

While such a temperature effect limits the amount of interpretation which one can give to rates of polymerization in this sort of study, it does provide a reasonable explanation for an inconsistency found in trying to cross calibrate dilatometers by comparing the rates of polymerization of a common initiated system. At the time the cross calibration was done, there was no confidence in the reproducibility of the thermal rate, so an ABN-initiated polymerization of styrene at 50° was chosen for a common calibration solution. The results are shown in Table 15.

It was felt that the disagreement between the above rates was outside the experimental error in the calibration of the dilatometers and the differences do, to a first approximation, seem to be ordered in the same direction as would be assigned upon consideration of heating effects.

One further result of these runs was the fact that there was no detectable deviation from linearity for the plot of these data (readings were taken every two to four minutes for the course of the run which was usually between one and two hours). While this result is certainly expected with the

Table 15. Results of cross calibration of dilatometers with a common 0.09507 M azo-bis-isobutyronitrile solution in undiluted styrene (8.45 M) solution at 50°

Run	Dilatometer designation	$R_p \times 10^4$ moles $l.^{-1}$ $sec.^{-1}$	Diameter[a] of volume cell cm.
23	NTB	0.8713	(3.2)[b]
24	V, VI	0.8432	2.26
25	I, II	0.8781	3.00
26	NTBC	0.8970	3.10
27	III, IV	(0.8638)[c]	3.00

[a] From Table 3.

[b] Estimated, as this dilatometer was destroyed before the measurement of its diameter had been made.

[c] The diameter of the capillary for this dilatometer was assumed to be the same as the precision bore tubing manufacturer's specifications.

dilatometers constructed from precision bore capillary tubing, it was of interest to have such a check for the dilatometers constructed of stock capillary tubing. Also, calibration using the expansion of mercury covered only about half the length of the capillaries for the dilatometers constructed from stock capillary tubing.

The effect of miscellaneous additives on the rate of azo-*bis*-isobutyronitrile-initiated polymerization of undiluted styrene at 70.0°

The effect of several miscellaneous additives upon the rate of initiated polymerization is presented in Table 16. In general the effects of these compounds were very small and, in view of the preceding discussion of temperature effects, no attempt will be made to comment on differences observed for the rates. It may be said that they were in general without effect although tetracyanoethylene probably is an exception. The fact that the tetracyanoethylene disappeared within ten minutes and that the last traces disappeared very sharply, suggests that it was consumed in a free radical reaction, perhaps copolymerization. It probably was not consumed by a direct reaction with styrene as a similar solution in styrene heated at a higher temperature in air retained the characteristic red color of tetracyanoethylene for a longer period of time.

Calculation of the rate constant for the decomposition of dimethyl-N-(2-cyano-2-propyl)-ketenimine from the decrease in rate of the ketenimine-initiated polymerization of styrene at 70.0°

It has been mentioned earlier in this section that with the ABN- and RR'-initiated styrene polymerization, the rate

Table 16. The rate of azo-bis-isobutyronitrile initiated styrene (8.28 M) polymerization at 70.0° in the presence of miscellaneous additives

Run	Dilatometer designation	Initial initiator molarity x 10^2	Additive	Initial additive molarity x 10^2	$R_p \times 10^4$ moles $l.^{-1}$ $sec.^{-1}$
20	NTB	1.00	none	-	2.121
21	NTBC	1.00	anthracene	0.545	1.950
22	NTBCL	1.00	phenanthrene	0.615	2.019
29	V, VI	1.001	chrysene	0.544	2.029
30	NTBCL	1.000	1,2-benzanthracene	0.544	2.138
31	I, II	1.000	fluoranthene	0.544	2.172
46	I, II	0.998	tetracyanoethylene[a]	0.549	2.23[a]
73	NTBCL	1.016	$Fe(DPM)_3$[b]	0.392	2.139[c]

[a] Red color disappeared sharply within ten minutes of start of run. Solution was yellowish thereafter.

[b] $Fe(DPM)_3$ = ferric chelate of dipivaloylmethane.

[c] Characteristic orange-red color persisted throughout the polymerization.

of polymerization decreases appreciably during a run due to the fact that the half-life for the two initiators is of the same order of magnitude as the length of the runs (Figure 1). The following analysis of the equations of polymerization indicated that from this decrease in slope, one should be able to calculate the first order rate constant for the initiator.

Equation 25 for first order decomposition of initiator was substituted into Equation 26, the general form of the rate of polymerization, giving Equation 27. The rate of polymerization determined dilatometrically is given by Equation 28. These two expressions for the rate of polymerization give Equation 29 when they are set equal to each other. Using Equation 29 and taking the ratio at two different times, t_1 and t_2, one finally obtains the rather simple expression, Equation 30. It should be noted that if Equation 26 contained a different dependence on monomer concentration, this treatment would still hold.

$$(25) \quad (I) = (I)_o \, e^{-kt}$$

in which (I) = initiator concentration.
$(I)_o$ = initial initiator concentration.
k = the first order rate constant for decomposition of initiator.
t = time.

$$(26) \quad R_p = k_p \frac{R_i^{\frac{1}{2}}}{2^{\frac{1}{2}} k_t^{\frac{1}{2}}} (M)$$

in which R_p = rate of polymerization.
k_p = rate constant for chain propagation.
R_i = rate of initiation.

k_t = rate constant for termination.

(M) = monomer concentration.

$$(27)\quad R_p = k_p \frac{(ak)^{\frac{1}{2}}}{k_t^{\frac{1}{2}}} (I)_o^{\frac{1}{2}} e^{-\frac{kt}{2}} (M)$$

in which a = initiator efficiency.

$$(28)\quad R_p = \frac{dX}{dD} \cdot \frac{2AD}{V} (M)^o \frac{dh}{dt}$$

in which X = mole fraction of monomer converted to polymer.

D = density of monomer solution.

A = area of one capillary.

V = calibrated volume of dilatometer.

$(M)^o$ = concentration of pure monomer.

k = level of the meniscus in the capillary.

$$(29)\quad k_r \frac{(ak)^{\frac{1}{2}}}{k_t^{\frac{1}{2}}} (I)_o^{\frac{1}{2}} e^{\frac{-kt}{2}} (M) = \frac{dX}{dD} \frac{2AD}{V} (M)^o \frac{dh}{dt}$$

$$(30)\quad e^{\frac{-k(t_2-t_1)}{2}} = \frac{\frac{dh}{dt}_2}{\frac{dh}{dt}_1}$$

in which t_i = time at point i.

$i = 1, 2, \ldots$

A preliminary calculation using data from a rather short run (one hour) gave a rate for the decomposition of ABN in fair agreement (30 per cent) with the value determined by nitrogen evolution. Analysis indicated that a longer run should yield a better value. To this end a run, Run 42, was made with RR' at low concentration, Run 42, (RR') equal to 4.15×10^{-4} M, in undiluted styrene and the results are tabulated in Table 17. The values of $\frac{dh}{dt}_{i}$ were obtained by plotting the data (cathetometer readings taken every two to four minutes over six hours) on a large roll of graph paper, drawing a smooth curve through the data, and differentiating graphically using a first surface mirror. Since the rate of polymerization in this run was low, it was necessary to correct for the thermal rate. This correction was made by subtracting the thermal rate, a constant, $\frac{dh}{dt}^{2}_{Th}$, from the square of the slopes obtained graphically, $\frac{dh}{dt}^{2}_{i}$. Figure 4 shows a plot of $\left[(\frac{dh}{dt})^2 - (\frac{dh}{dt})^2_{Th}\right]_i$ versus time.

The data were fitted to a linear least squares regression which gave the following value for the first order rate constant of the decomposition of RR':

$$k = 7.16 \times 10^{-5} \pm 1.65 \times 10^{-5} \quad \text{99 per cent confidence}^{123}$$

$$\pm 1.21 \times 10^{-5} \quad \text{95 per cent confidence}^{123}$$

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[123] Standard deviation = 0.574 computed from the formula for standard deviation[124]. The confidence limits for 99 and 95 per cent were determined by multiplying this standard deviation by 2.878 and 2.101 respectively obtained from a table of the student t distribution for 18 samples.

[124] G. Tintner, "Econometrics", p. 29, John Wiley and Sons, Inc. New York (1952).

Figure 4. Determination of the rate of decomposition of dimethyl-N-(2-cyano-2-propyl)-ketenimine from the decrease in the rate of polymerization of the ketenimine-initiated styrene (8.28 M) at 70.0°

Ordinate: $\log_{10}\left[\left(\frac{dh}{dt}\right)^2 - \left(\frac{dh}{dt}\right)^2_{Th}\right]^{-1}_{i}$

Abscissa: time in seconds

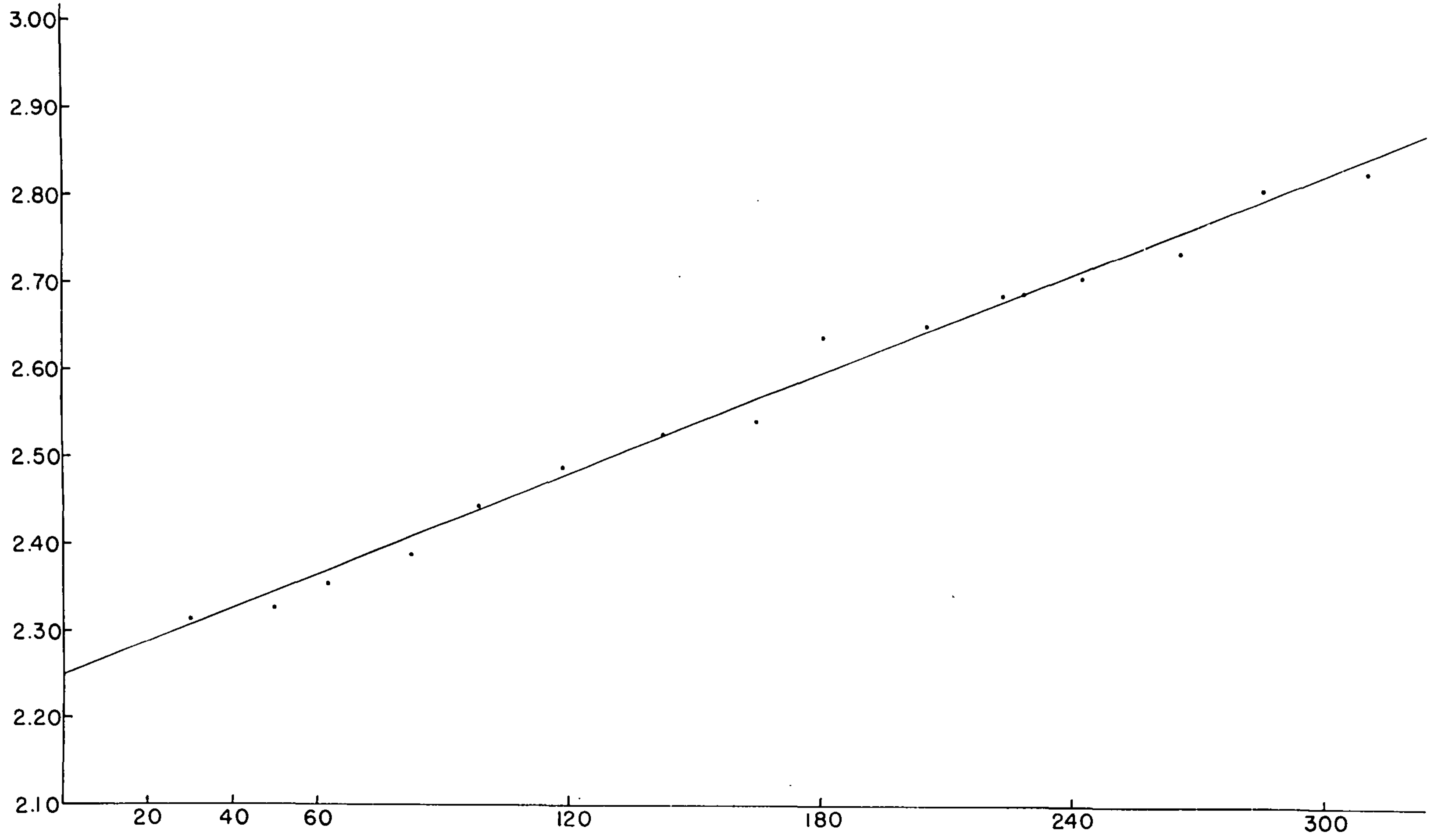
3.00
2.90
2.80
2.70
2.60
2.50
2.40
2.30
2.20
2.10
20
40
60
120
180
240
300

Table 17. Determination of the rate of decomposition of dimethyl-N-(2-cyano-2-propyl)-ketenimine from the decrease in the rate of ketenimine-initiated polymerization of styrene

Time minutes	$(\frac{dh}{dt})_i \times 10^2$ cm.min.$^{-1}$	$\left[(\frac{dh}{dt})^2 - (\frac{dh}{dt})^2_{Th}\right]^a_i$ x 10^4 cm.^{2}min.$^{-1}$	$\log_{10}\left[(\frac{dh}{dt})^2 - (\frac{dh}{dt})^2_{Th}\right]^{-1}_i$
39.66	7.017	48.539	2.31387
49.72	6.910	47.049	2.32736
63.22	6.702	44.218	2.35449
83.20	6.460	41.033	2.38686
98.65	6.056	35.976	2.44404
119.28	5.760	32.479	2.48841
143.20	5.536	29.948	2.52362
165.36	5.434	28.829	2.54020
180.64	4.870	23.018	2.63789
206.08	4.803	22.370	2.65031
224.01	4.618	20.627	2.68556
229.12	4.612	20.572	2.68673
243.04	4.513	19.668	2.70621
266.21	4.363	18.337	2.73664
286.12	4.037	15.598	2.80693
310.78	3.947	14.880	2.82737
334.40	3.873	14.301	2.84460
357.21	3.648	12.609	2.89933

[a] $(\frac{dh}{dt})_{Th}$ = 0.00836 cm. min.$^{-1}$ for dilatometer I, II.

This value of k considering the scatter lies close to the value found by quantitative infrared in this investigation, 6.1×10^{-5} sec.$^{-1}$ and the value found by Trapp[125] 7.1×10^{-5} sec.$^{-1}$.

Rate of Decomposition of Azo-Bis-Isobutyronitrile by Nitrogen Evolution and Spectrophotometry

The rate of decomposition of azo-*bis*-isobutyronitrile (ABN) was determined in benzene by the rate of nitrogen evolution for 15 runs which are tabulated in Table 18. The rate constants were determined graphically by plotting $\log_{10} (V_{\infty} - V_t)$ versus time. V_t is the volume recorded at time, t, and V_{∞} is the volume at infinite time calculated from the weight of ABN used in the run and the initial volume reading taken on the apparatus.

These plots were quite linear with little scatter even though volume readings were sometimes taken as frequently as every three minutes. Consequently the volume data are not included in this thesis with only the first order rate constants included in Table 18. It should be noted that a correction was applied to the initial volume reading to compensate for the amount of nitrogen evolved before the first read-

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[125] O. D. Trapp, *op. cit.*, p. 86.

Table 18. The rate of decomposition of azo-bis-isobutyronitrile in benzene solution at 70.0°

Run	Initial weight of $ABN^{d,f}$ $\times 10^3$ gm.	Source $ABN^{d,e}$	$k_{N_2}{}^a$ $\times 10^5$ $sec.^{-1}$	$k_{tot.N_2}{}^b$ $\times 10^5$ $sec.^{-1}$	$k_{U.V.}{}^c$ $\times 10^5$ $sec.^{-1}$	Wave length of determination of $k_{U.V.}$ Å	Stirring rate	Time interval over which k_{N_2} calculated min.
X'	174.7	1	4.65				slow	0-110
XI'	240.5	1	4.29				slow	0-110
XIII	214.5	1	4.20				slow	0.65
XIV	236.3	1	4.81				slow	0.50

[a] First order rate constant determined by rate of nitrogen evolution.

[b] First order rate constant determined by total nitrogen evolved during the length of the run.

[c] First order rate constant determined by ultraviolet measurement of absorbancy after the run and calculation of absorbancy before the run using the weight of ABN used.

[d] ABN = azo-bis-isobutyronitrile.

[e] Source 1 refers to ABN recrystallized twice from methanol. Ultraviolet measurement of the absorbancy at 3450A of six samples of this source showed them to be uniform within 1 per cent. Source 2 refers to ABN from source 1 recrystallized such as to give fine crystals. Both sources showed the same extinction coefficient at 3450Å.

[f] Amount of benzene = 6.0 ml. in all runs.

Table 18. (Continued)

Run	Initial weight of ABN $\times 10^3$ gm.	Source ABN	k_{N_2} $\times 10^5$ sec.$^{-1}$	$k_{tot.N_2}$ $\times 10^5$ sec.$^{-1}$	$k_{U.V.}$ $\times 10^5$ sec.$^{-1}$	Wave length of determination of $k_{U.V.}$ Å	Stirring rate	Time interval over which k_{N_2} calculated min.
			4.64				slow	50-130
XV	217.9	2	4.30				slow	0-75
XVI	198.8	2	4.20				slow	0-85
XVII	188.0	2	3.92				slow	0-80
XVIII	257.3	2	4.12				slow	70-130
			4.32				fast	0-60
XIX	215.1	2	-				fast	0-60
			4.34				slow	60-140
			4.20[g]				fast	140-190
XX	228.1	2	4.52				fast	0-60

---

[g] It should be noted that although the rate in the faster stirred period was slower, there did occur a desaturation of the nitrogen in the solution as was evidenced by a well defined discontinuity in the logarithmic plot of the volume data.

Table 18. (Continued)

Run	Initial weight of ABN $\times 10^3$ gm.	Source ABN	k_{N_2} $\times 10^5$ sec.$^{-1}$	$k_{tot.N_2}$ $\times 10^5$ sec.$^{-1}$	$k_{U.V.}$ $\times 10^5$ sec.$^{-1}$	Wave length of determination of $k_{U.V.}$ Å	Stirring rate	Time interval over which k_{N_2} calculated min.
XXI	218.4	2	4.19	4.37	3.41[h]	3450	fast	0-175
XXII	201.7	2	4.26	4.34	3.26[h]	3450	fast	0-175
XXIII	221.2	2	4.32	4.14	3.39[h]	3450	fast	30-204
XXIV	206.9	2	4.08	4.16[i]	3.36[h]	3450	fast	0-170
					3.42	3500		
					3.60	3600		
					3.68	3700		
					3.78	3800		
	209.2	2	4.10	4.13[i]	3.36[h]	3450	slow	0-210

---

[h] A degassed (fore pump) run, Run 85, in which ABN was decomposed in sealed tubes gave, by the ultraviolet method at 3460Å, a rate constant of 3.34×10^{-5} sec.$^{-1}$ in good agreement with these "one point" values.

[i] This rate constant represents equally well (within 1 per cent) the volume change observed at 70° (with slight warm up correction of 3 minutes) and the volume change measured at 25°.

Table 18. (Continued)

Run	Initial weight of ABN $\times 10^3$ gm.	Source ABN	k_{N_2} $\times 10^5$ sec.$^{-1}$	$k_{tot.N_2}$ $\times 10^5$ sec.$^{-1}$	$k_{U.V.}$ $\times 10^5$ sec.	Wave length of determination of $k_{U.V.}$ Å	Stirring rate	Time interval over which k_{N_2} calculated min.
					3.61	3500		
					3.76	3600		
					3.56	3700		
					3.92	3800		

ing was taken (usually around ten minutes). In the calculation of V_{∞} this correction was small (around 3 per cent).

In some runs further estimates were made of the rate of ABN decomposition by measuring both the total nitrogen evolved and the optical density decrease during the run. These values are also tabulated in Table 18. Since the rate constants themselves show quite a bit of scatter, many experimental observations of a procedural nature are noted in Table 18. In all experiments, the temperature of the reaction cell was checked with a thermistor after the run to make sure that the cell was at 70.0°.

In Table 19 are tabulated the rates of decomposition of ABN in styrene determined by nitrogen evolution. The spectrophotometric determination of ABN decomposition in styrene was not practical[126] and so the data consist only of the nitrogen evolution data. While the temperature measurements of the reaction cell were not made after the experiment as was done with the runs in Table 18, a later experiment indicated that the temperature of Runs IX, X, and XI was very close to 70.0°. An experiment done with monomer in the absence of ABN showed that the temperature of the cell was 0.9° below that of the bath used to heat the cell; however, a later experiment showed that the addition of the amount of ABN used in a run increased

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[126] Light scattering from polymer formed interferes with the ultraviolet measurements.

Table 19. The rate of decomposition of azo-bis-isobutyronitrile in styrene solution at 70.0°

Run	Initial weight of ABN[b,d]	Source ABN[b,c]	k_{N_2}[a] x10^5 sec.$^{-1}$	Stirring rate	Time interval over which k_{N_2} calculated, min.
IX	179.3	1	4.41	slow	0-65[e]
X	179.2	1	4.53	slow	0-55[e]
XI	181.3	1	4.56	slow	0-55[e]
XII	207.7	1	4.65	slow	0-60[e]

[a] First order rate constant determined by rate of nitrogen evoluation.

[b] ABN = azo-bis-isobutyronitrile.

[c] Recrystallized twice from methanol.

[d] Amount of styrene = 6.0 ml. in all runs.

[e] Solution became too viscous to permit uniform stirring rate.

the temperature of the stirred cell about 1°. These thermistor experiments were done in the presence of air.

In calculations using the rate of decomposition of ABN, the value 4.25×10^{-5} sec.$^{-1}$ was used for pure benzene and 4.56×10^{-5} sec.$^{-1}$ for pure styrene. The rate constants for solutions of the two solvents were estimated by a linear interpolation with respect to monomer concentration.

The Rate of Decomposition of Dimethyl-N-(2-Cyano-2-Propyl)-Ketenimine in Various Solutions at 62.5° and 70.0°

The rate of decomposition of dimethyl-N-(2-cyano-2-propyl)-ketenimine (RR') was required under a variety of conditions for this investigation. The results of a series of decompositions of RR' in various solutions at 62.5° and 70.0° in the presence of several additives are given in Tables 20, 21, and 22. All rate constants were determined by following the rate of disappearance of RR' by the quantitative infrared technique. When additives were present, blank scans of the wave number region around 2020 $cm.^{-1}$ were made to make sure that these additives did not interfere with the RR' analysis. The determination of the first order rate constants was done graphically. However, since the infrared data scatter much more on a first order rate plot than the nitrogen evolution data, the absorbancies are included in the tables.

A smooth curve was drawn through the data of Table 21 in which the dependence of the rate of decomposition of RR' on styrene molarity is tabulated. The rates at 8.28 M and 5.79 M were considered to be the same within experimental error and the curve was drawn flat in this region such that it averaged the two values. Values at other monomer concentration were extrapolated from this curve and are cited as extrapolated when used.

Table 20. The rate of decomposition of dimethyl-N-(2-cyano-2-propyl)-ketenimine in cumene solutions of carbon tetrachloride at 62.5° and cumene solutions of benzene at 70.0° both in the presence and absence of di-t-butyl-p-cresol and oxygen

Run	Solvent	Initial RR'[c] molarity x10^2	Initial DTBC[d] molarity x10^2	Reaction condition	Reaction time, hours	A[a]	k[b] x10^5 $sec.^{-1}$	Temperature °C
80	CCl_4[e]	1.04	-	*in vacuo*	1.50	0.621	0.84	62.5
					5.30	0.564		
					9.22	0.498		
					12.37	0.437		
					20.43	0.337		
					24.27	0.316		
					27.75	0.286		
					32.70	0.243		
					36.33	0.216		
					43.75	0.178		
					49.55	0.159		
					54.35	0.139		

---

[a] Infrared absorbancy determined both on Perkin Elmer Model 13 and Perkin Elmer Model 112 at 2020 $cm.^{-1}$.

[b] First order rate constant for disappearance of RR'.

[c] RR' = dimethyl-N-(2-cyano-2-propyl)-ketenimine.

[d] DTBC = di-t-butyl-p-cresol.

[e] Carbon tetrachloride.

Table 20. (Continued)

Run	Solvent	Initial RR' molarity x10^2	Initial DTBC molarity x10^2	Reaction condition	Reaction time, hours	A	k x10^5 sec.$^{-1}$	Temperature °C
79	2 CCl_4: 1 Cumene[f]	1.10	-	*in vacuo*	1.50	0.651[g]	0.96	62.5
					5.30	0.573[g]		
					9.22	0.494[g]		
					12.37	0.334		
					20.43	0.466		
					24.27	0.393		
					27.75	0.264[g]		
					32.70	0.304		
84	2 CCl_4: 1 Cumene	1.22	-	*in vacuo*	1.00	0.720	0.97	62.5
					4.12	0.651		
					7.28	0.588		
					12.85	0.465		
					23.78	0.325		
					27.63	0.285		
					32.05	0.251		
					38.22	0.195		
71	2 CCl_4: 1 Cumene	1.20	1.43	O_2	0.22	0.710	0.92	62.5
					1.83	0.665		
					3.58	0.607		
					4.22	0.603		
					5.50	0.575		
					6.17	0.532		
					7.00	0.552		

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[f] A mixture of the above proportions by volume made up at room temperature.

[g] Only these points were used in determining slope for this run.

Table 20. (Continued)

Run	Solvent	Initial RR' molarity x10^2	Initial DTBC molarity x10^2	Reaction condition	Reaction time, hours	A	k x10^5 sec.$^{-1}$	Temperature °C
					12.42	0.459		
					13.98	0.425		
					15.85	0.377		
					18.00	0.383		
					20.00	0.371		
					22.00	0.337		
					24.50	0.310		
					27.75	0.285		
72	2 CCl_4: 1 Cumene	1.20	2.33	O_2	0.25	0.710	1.01	62.5
					1.83	0.650		
					3.58	0.598		
					4.27	0.586		
					5.50	0.567		
					6.17	0.561		
					7.00	0.543		
					12.53	0.452		
					14.10	0.429		
					15.97	0.423		
					18.00	0.388		
					20.00	0.348		
					22.00	0.322		
					24.50	0.296		
					27.75	0.261		
78	2 CCl_4: 1 Cumene	1.53	1.12	O_2	0.58	0.637	0.93	62.5
					4.43	0.556		
					7.22	0.514		
					10.72	0.459		

Table 20. (Continued)

Run	Solvent	Initial RR' molarity $x10^2$	Initial DTBC molarity $x10^2$	Reaction condition	Reaction time, hours	A	k $x10^5$ $sec.^{-1}$	Temperature °C
					12.62	0.426		
					22.42	0.313		
					24.70	0.294		
					29.08	0.242		
					33.13	0.209		
					36.42	0.186		
					44.38	-		
					47.90	0.128		
96	Benzene	0.71	-	*in vacuo*	0.37	0.357	3.92	70.0
					1.37	0.307		
					2.60	0.244		
					3.58	0.216		
					4.90	0.177		
					5.87	0.153		
					6.97	0.123		
					8.33	0.106		
92	2 Benzene: 1 Cumene	1.27	-	*in vacuo*	0.40	0.638	3.49	70.0
					1.39	0.593		
					2.60	0.492		
					3.58	0.424		
					4.90	0.278		
					5.87	0.371		
					6.97	0.238		
					8.35	0.328		
90	2 Benzene: 1 Cumene	1.35	0.92	O_2	0.65	0.679	2.94	70.0
					1.68	0.600		

Table 20. (Continued)

Run	Solvent	Initial RR' molarity $\times 10^2$	Initial DTBC molarity $\times 10^2$	Reaction condition	Reaction time, hours	A	k $\times 10^5$ sec.$^{-1}$	Temperature °C
					2.35	0.562		
					3.02	0.521		
					3.73	0.485		
					5.15	0.414		
					5.75	0.408		
					7.23	0.348		
					8.28	0.325		
					9.28	0.301		
					10.57	0.303		
91	2 Benzene: 1 Cumene	1.30	1.92	O_2	0.60	0.652	2.90	70.0
					1.62	0.576		
					2.30	0.542		
					2.98	0.500		
					3.68	0.474		
					5.10	0.403		
					5.67	0.383		
					7.20	0.338		
					8.22	0.302		
					9.25	0.253		
					10.53	0.234		

Table 21. The rate of decomposition of dimethyl-N-(2-cyano-2-propyl)-ketenimine in styrene, benzene, and two styrene-benzene solutions at 70.0° *in vacuo*

Run	Styrene molarity in benzene solutions	Initial RR'[c] molarity $\times 10^2$	Reaction time, hours	A[a]	k[b] $\times 10^5$ sec.$^{-1}$
93	8.28[d]	1.51	.167	0.542	6.22
			.400	0.506	
			.683	0.488	
			.917	0.449	
			1.20	0.420	
			1.42	0.413	
			1.68	0.389	
94	5.79	1.05	.1666	0.514	6.31
			.350	0.494	
			.516	0.477	
			.667	0.465	
			.833	0.441	
			1.000	0.435	
			1.167	0.415	
			1.333	0.401	
			1.500	0.376	
			1.667	0.367	
			1.833	0.352	
95	2.59	1.56	.183	0.808	5.41
			.366	0.779	
			.500	0.757	
			.667	0.735	
			.833	0.702	
			1.000	0.679	
			1.333	0.662	
			1.500	0.643	

---

[a] Infrared absorbancies determined on the Perkin Elmer Model 13 at 2020 cm.$^{-1}$.

[b] First order rate constant for disappearance of RR'.

[c] RR' = dimethyl-N-(2-cyano-2-propyl)-ketenimine.

[d] Molarity of undiluted styrene at 70.0°.

Table 21. (Continued)

Run	Styrene molarity in benzene solutions	Initial RR' molarity x10^2	Reaction time, hours	A	k x10^5 sec.$^{-1}$
			1.667 0	0.618 0.830	
96	0.00	0.71	-[e]	-[e]	3.92

[e] Reported in Table 20, p. 136.

Table 22. The rate of decomposition of dimethyl-N-(2-cyano-2-propyl)-ketenimine in carbon tetrachloride solution at 62.5° *in vacuo* in the presence of diphenylpicrylhydrazyl and the aluminum and the ferric chelates of dipivaloylmethane

Run	Initial RR'[c] molarity x10^2	Additive	Additive molarity x10^2	Reaction time, hours	A[a]	k[b] x10^5 sec.$^{-1}$
80	1.04	none	-	-[d]	-[d]	0.84
81	1.04	DPPH[e,f]	0.0405[g]	1.50	.599	1.00

---

[a] Infrared absorbancy as determined on the Perkin Elmer Model 112.

[b] First order rate constant for disappearance of RR'.

[c] RR' = dimethyl-N-(2-cyano-2-propyl)-ketenimine.

[d] Reported in Table 20, p. 136.

[e] DPPH = diphenylpicrylhydrazyl.

[f] Sample left opened (but corked) under dry ice for one month.

[g] This concentration exceeded the solubility at room temperature so solutions were of somewhat lower concentration than indicated above.

Table 22. (Continued)

Run	Initial RR' molarity x10^2	Additive	Additive molarity x10^2	Reaction time, hours	A	k x10^5 sec.$^{-1}$
				5.30	.537	
				9.22	.457	
				12.37	.402	
				20.43	.295	
				24.27	.264	
				27.75	.228	
				32.70	.197	
82	1.09	Fe(DPM)$_3^h$	0.00522	1.50	.646	0.85
				5.30	0.560	
				9.22	.498	
				12.37	.455	
				20.43	.359	
				24.27	.305	
				27.75	.288	
				32.70	.253	
83	1.09	Al(DPM)$_3^i$	0.00522	1.50	0.634	0.805
				5.30	0.570	
				9.22	0.513	
				12.37	0.459	
				20.43	0.363	
				24.27	0.327	
				27.75	0.314	
				32.70	0.252	

[h] Fe(DPM)$_3$ = ferric chelate of dipivaloylmethane.

[i] Al(DPM)$_3$ = aluminum chelate of dipivaloylmethane.

Rate of Formation of Dimethyl-N-(2-Cyano-2-Propyl)-Ketenimine from Azo-Bis-Isobutyronitrile in Styrene and Benzene at 70.0°

The initial rate of formation of dimethyl-N-(2-cyano-2-propyl)-ketenimine (RR') from azo-*bis*-isobutyronitrile (ABN) has been measured at 70.0° in styrene and benzene and the results are shown in Table 23. The infrared method of analysis for RR' was used. Since the absorbancy of RR' is fairly insensitive to solvent change (differences probably being due to changes in index of refraction with solvent), values of the extinction coefficient determined in carbon tetrachloride were used both with styrene and benzene.

Runs 87 and 89 do not show very good precision, however, Run 89 is probably more accurate as care was taken to cool samples very quickly and special care was taken making the infrared measurements.

The Efficiency of Radical Production from Dimethyl-N-(2-Cyano-2-Propyl)-Ketenimine as Measured in the Air Oxidation of Cumene

The efficiency of radical production from dimethyl-N-(2-cyano-2-propyl)-ketenimine (RR') was measured by observing the induction period in the oxidation of cumene in carbon tetrachloride solution in the presence of an antioxidant, di-_t_-butyl-_p_-cresol. This method was developed and used for this system and a large number of similar ones by Hammond, Sen, and Boozer[127] for the initiator azo-_bis_-isobutyronitrile (ABN). The induction period in the uptake of oxygen was

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[127] G. S. Hammond, J. N. Sen, and C. E. Boozer, _J_. _Am_. _Chem_. _Soc_., _77_, 3244 (1955).

Table 23. The initial rate of formation of dimethyl-N-(2-cyano-2-propyl)-ketenimine from azo-bis-isobutyronitrile in benzene and styrene at 70.0° *in vacuo*

Run	Initial ABN[b] molarity $\times 10^2$	Solvent	Reaction time, hours	A[a]	$R_{f_{RR'}}$ $\times 10^6$ moles $l.^{-1}$ $sec.^{-1}$ [c]	$R_{d_{ABN}}$ $\times 10^6$ moles $l.^{-1}$ $sec.^{-1}$ [d]	$\frac{R_{f_{RR'}}}{R_{d_{ABN}}}$
97	4.23	benzene	0.52	.079	1.29	1.8	0.72
			1.18	0.177			
			2.00	0.260			
			3.85	0.376			
			4.53	0.394			
			5.00	0.398			
			5.67	0.423			
			6.47	0.432			
			7.03	0.439			
			7.62	0.426			
87	4.36	styrene	0.23	0.037	0.8	2.0	0.39
			0.40	0.045			
			0.58	0.066			
			0.74	0.070			
			0.90	0.091			
			1.10	0.103			
			1.30	0.108			
			-	0.125			
89	4.31	styrene	0.15	0.025	0.51	2.0	0.26
			0.33	0.035			
			0.52	.046			
			0.67	.063			
			0.83	.078			
			1.00	.090			
			1.16	.107			
			1.40	.117			

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[a] Infrared absorbancy determined with the Perkin Elmer Model 13.

[b] ABN = azo-bis-isobutyronitrile.

[c] Initial rate of formation of dimethyl-N-(2-cyano-2-propyl)-ketenimine (RR').

[d] Initial rate of decomposition of ABN.

observed using the gas apparatus. The results are tabulated in Table 24 for two runs of ABN and two runs of RR'.

In these runs, the temperature of the water bath was set at 62.5°, so the temperature of the reaction cell was probably at a somewhat lower temperature (a few tenths of a degree) than 62.5°.

The results are not extremely precise, but, the _a_ value of ABN agree well with the result of Hammond _et al_.[127] of 0.46 from iodine scavenging experiments in carbon tetrachloride. The ratio of the efficiency factors of RR' to ABN is 0.64.

Table 24. The efficiency of radical production from dimethyl-N-(2-cyano-2-propyl)-ketenimine and azo-*bis*-isobutyronitrile in carbon tetrachloride at 62.5° as measured by the air oxidation of cumene

Run	Initiator	Initial number of moles of initiator x10^3	Initial number of moles of di-*t*-butyl-*p*-cresol x10^5	Induction period min.	Efficiency factor[a,b]
IV	ABN[c]	0.619	1.35	66	0.469
VI	ABN	0.614	1.35	62	0.514
VII	ABN	0.612	1.47	67.6	0.511
V[d]	RR'[e]	0.648	1.35	133	0.281
VIII	RR'	0.338	1.47	200	0.362

[a] Calculated using the rate of decomposition of azo-*bis*-isobutyronitrile and dimethyl-N-(2-cyano-2-propyl)-ketenimine as 1.18×10^{-5} sec.$^{-1}$ and 0.97×10^{-5} sec.$^{-1}$ respectively.

[b] Calculated using the formula $2(\mathrm{DTBC})_o = 2a(\mathrm{I})_o(1-e^{-kT})$ in which $(\mathrm{DTBC})_o$ = initial di-*t*-butyl-*p*-cresol concentration, $(\mathrm{I})_o$ = initial inhibitor concentration, k = rate of decomposition of initiator, a = efficiency factor for the initiator, T = time of the induction period.

[c] ABN = azo-*bis*-isobutyronitrile.

[d] Temperature of this run fell to 60° for 14 minutes during induction period. Effect probably negligible.

[e] RR' = dimethyl-N-(2-cyano-2-propyl)-ketenimine.

DISCUSSION

Preliminary Remarks

The initial objective of this investigation was to determine the efficiency of radical production from azo-bis-isobutyronitrile (ABN) as a function of monomer concentration in the polymerization of styrene by the method of inhibitors. Early experiments indicated the possibility that, in the case of styrene-benzene solutions using chloranil as an inhibitor, the efficiency of initiation varied with monomer concentration. The work was therefore extended to include another initiator, several other inhibitors, and an attempt was also made to estimate the efficiency from the rate of uninhibited polymerizations. Since estimation of relative efficiencies by either method is based on an accurate knowledge of the rate of decomposition and purity of the initiator, the results of studies of these variables are discussed in some detail first. With the inhibitor method, the purity of the inhibitor is of equal importance of course. However, the inhibitors used are fairly stable, were readily purified by recrystallization, and seemed well characterized by their melting points. Similar remarks apply to the initiator, ABN. Finally, the various measures of efficiency are compared and a mechanistic conclusion is suggested.

Purity of Dimethyl-N-(2-Cyano-2-Propyl)-Ketenimine

While Trapp's[128] assay of dimethyl-N-(2-cyano-2-propyl)-ketenimine (RR') with iodine probably is accurate, the method is not very precise (± 5 to 10 per cent), perhaps because an eight-fold excess of iodine was used. Of the four methods tried in this investigation, only the titration of RR' with bromine in carbon tetrachloride was reproducible and precise. Results from bromine titrations were taken as the standard for calibration of optical data.

In the titration of RR' with hydrobromic acid in acetic acid no titer was obtained when the samples were initially dissolved in glacial acetic acid. This result may indicate that acetic acid reacts directly with RR'. Small amounts of water in the acetic acid could, however, give the same effect. Titrations with hydrobromic acid and perchloric acid perhaps involve a loose adduct which can undergo elimination reactions in the presence of a stronger base. It is surprising that the perchloric acid method gives a value (upon long standing) very close to the value assigned by the bromine method.

The data in Table 2, p. 78, probably represent the best values thus far obtained for extinction coefficients of RR' in the ultraviolet and infrared. It should be noted that the

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[128] O. D. Trapp, Unpublished Ph.D. Thesis, p. 39, Iowa State College Library, Ames, Iowa (1957).

direction of the differences between the values of specific absorbancy in the infrared in cyclohexane and carbon tetrachloride are inconsistent when compared between the two infrared instruments used and outside the experimental error expected of quantitative infrared analyses (± 3 per cent). However, the cyclohexane solutions were too concentrated to be in the region of maximum sensitivity of the densitometer and the measurements were probably inaccurate. The relation of ultraviolet absorbancy measurements in cyclohexane to infrared absorbancy in carbon tetrachloride is the most important result for the present investigation. Since the infrared peaks in cyclohexane have never been used as a standard, this data has not been rechecked.

The data in Table 1, p. 74, indicate that specific absorbances as determined by ultraviolet analysis are more reliable for estimation of purity of relatively pure[129] RR' fractions than is the infrared method. The reason for this is not clear as the kinetic data within a run in Trapp's[130] work and in this work usually do not scatter more than ± 3 per cent. Differences in the infrared data are as great as ± 15 per cent. In addition, the data in the table indicate that the specific absorbancies determined for a given infrared instru-

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[129] Any yellowing due to oxidation of RR' seriously interferes with the ultraviolet method.

[130] O. D. Trapp, op. cit.

ment may vary from day to day. It is suggested this variation is due to variable sensitivity of the instrument. This effect could arise from misalignment of the optics or could be electronic in nature.

The Rate of Decomposition of Azo-Bis-Isobutyronitrile

The results of fifteen determinations of the rate of decomposition of azo-bis-isobutyronitrile (ABN) in benzene at 70° are shown in Table 18, p. 129, and the results of four determinations of the same rate in styrene are shown in Table 19, p. 134. In all of the runs the rate was determined by the rate of nitrogen evolution. In addition, in five of the runs the total amount of nitrogen evolved was measured, and in two of these runs the decrease in absorbancy at 2800Å was observed providing independent checks for the values of the rate constants determined by nitrogen evolution.

Examination of the Tables 18 and 19 show that the results scatter from the mean by as much as ± 10 per cent in the case of benzene and ± 4 per cent in the case of styrene. If one considers a typical run to last 60 minutes, the maximum error which one would expect (using the total differential as an estimate of the maximum error method), assuming volumes may be measured to ± 0.1 ml. and times to ± 10 seconds, is ± 5 per cent. If the runs were 120 minutes, the expected error would decrease to ± 3 per cent. Since temperature was controlled to at least ± 0.1° in a given solvent, other variables were investigated. Runs XVIII and XIX indicate that the rate of stirring does not give a unique effect although it is interesting to note that there is less scatter among the runs carried out with rapid stirring than among the other runs. Finally, Run XIV indicates that, while light may accelerate decomposition, the effect is small (3 per cent). Explanation for the scatter lacks any sound basis. One possibility is that small, varying amounts of oxygen are contained in the system. Efforts were made to establish a rigorously reproducible procedure. However, the apparatus was connected with many pieces of Tygon tubing (wired) and only a Fieser Train was used to purify the nitrogen.

Weighted average values for the rate in benzene and styrene are 4.25×10^{-5} sec.$^{-1}$ and 4.56×10^{-5} sec.$^{-1}$ respectively. At the time of the experiments it was thought that the experiments in styrene (with the exception of Run XII) involved a lower temperature (by 0.7 to 1.3°) than the benzene runs since the temperature in the reaction cell was not adjusted to 70.0° with the thermistor. However, it was observed later using a thermistor that a stirred ABN solution of styrene has a temperature around 1° higher than that of uninitiated, stirred styrene at 70.0°. Thus, the above values will be used for the respective rates at 70.0°. It seems reasonable to expect that the dependence of rate of decomposition of ABN is a fairly insensitive function of solvent composition since benzene and styrene are quite similar and since the first step in the decomposition of ABN is almost certainly not reversible.

Rate of Decomposition of Dimethyl-N-(2-Cyano-2-Propyl)-Ketenimine

Table 21, p. 141, shows that the dependence of the rate of decomposition of dimethyl-N-(2-cyano-2-propyl)-ketenimine (RR') on the concentration of styrene in benzene increases monotonically[131]. The magnitude of the difference, 50 per cent, is striking when compared with the results obtained with ABN (10 per cent increase). The qualitative experiments conducted with a thermistor indicated that the temperature of an unstirred styrene solution containing 0.015 M ABN would be at most 2° higher than the bath. Since the activation energy of RR' decomposition in benzene is 28.9 kcal./mole[132], one can readily show that 0.1° difference in temperature should give a 1 per cent difference in the value for the first order rate constant. The mechanism proposed by Trapp[133] for the decompo-

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[131] The rate constants for Runs 93 and 94 are considered to be equal within experimental error.

[132] O. D. Trapp, Unpublished Ph.D. Thesis, p. 85, Iowa State College Library, Ames, Iowa (1957).

[133] *Ibid.*, p. 102.

sition of RR' in the absence of scavenger is as follows:

(1) $\mathrm{RR'} \xrightarrow{k_1} \overline{2\mathrm{R}\cdot}$

(2) $\overline{2\mathrm{R}\cdot} \xrightarrow{k_2} \mathrm{RR}$

(3) $\overline{2\mathrm{R}\cdot} \xrightarrow{k_3} \mathrm{RR'}$

(4) $\overline{2\mathrm{R}\cdot} \xrightarrow{k_4} 2\mathrm{R}\cdot$

(5) $2\mathrm{R}\cdot \xrightarrow{k_5} \overline{2\mathrm{R}\cdot}$

in which RR = tetramethylsuccinonitrile
$2\mathrm{R}\cdot$ = two "free" cyanopropyl free radicals
$\overline{2\mathrm{R}\cdot}$ = two "caged" cyanopropyl free radicals

If one ascribes the 30 per cent increased rate in styrene to complete scavenging of caged radicals by monomer (Equation 6), 23 per cent of the RR' dissociated returns by Reaction 3 to regenerate RR'. This estimate agrees well with a similar estimate from Trapp's work[134] of 18 per cent return. However, such a change in efficiency with monomer concentration is in opposition to current views[135,136,137] of the ability of mono-

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[134] *Ibid.*, p. 85, p. 106.

[135] P. J. Flory, "Principles of Polymer Chemistry", p. 120, Cornell University Press, Ithaca, N. Y. (1953).

[136] J. C. Bevington, *Trans. Faraday Soc.*, *51*, 1302 (1955).

[137] C. Walling, "Free Radicals in Solution", p. 77, John Wiley and Sons, Inc., New York (1957).

mer to scavenge from the cage. These views are based on the velocity with which monomer radicals add to monomer and the comparatively short time in which diffusion of radicals out of the cage takes place. One argument against these views would be to point out that the addition of cyanopropyl radical to monomer should be a much faster process than the addition of monomer radical to monomer.

(6) $\overline{2R\cdot} + M \longrightarrow R\cdot + M\cdot$

in which M = monomer molecule

$M\cdot$ = monomer radical

A parallel argument is suggested by Hammond's proposal[138] that reversible molecular complexes with radicals are important in inhibition of autoxidations. In this case alkoxy radicals are suggested to form "pi" complexes with electron-rich aromatic-amines. In the case at hand, if the comparatively electrophilic cyanopropyl radical were to form a molecular complex with an electron rich system such as styrene, the scavenging from the cage by monomer could be explained quite reasonably, Equations 7 and 8.

(7) $\overline{2R\cdot} + M \rightleftarrows \overline{R\cdot + M{:}R\cdot}$

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[138] G. S. Hammond, C. E. Boozer, C. E. Hamilton, and J. N. Sen, *J. Am. Chem. Soc.*, *77*, 3238 (1955).

$$(8) \qquad R\cdot + M{:}R\cdot \xrightarrow{\text{Diffusion}} R\cdot + M{:}R\cdot$$

in which M:R• = a pi complex between monomer, M, and primary initiator radical, R•

In Table 20, p. 136, one can see that at 62.5° the rate of decomposition of RR' in a 1:2 cumene-benzene mixture is the same under nitrogen and in oxygen in the presence of di-*t*-butyl-*p*-cresol. Oxygen is certainly an efficient scavenger of "free" free radicals[139], so one would expect return by step (5) in the above mechanism to be inhibited and that the rate of disappearance of RR' should be increased correspondingly. The efficiency of R-R' which was obtained in the air oxidation experiment, Table 24, p. 147, is 40 per cent above that inferred from the increase in the rate of decomposition in styrene. Therefore, the overall rate of decomposition of RR' would be expected to be increased by at least 8 per cent. Decomposition in the presence of oxygen did not indicate such an increase. The difference could lie within the experimental error of the determination of the rate constants. The rate was apparently increased by about 20 per cent in the presence of diphenylpicrylhydrazyl.

Runs 80 and 82 in Table 22, p. 142, are interesting as they show that the effect on the rate of decomposition of RR'

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[139] G. S. Hammond, J. N. Sen, and C. E. Boozer, *J. Am. Chem. Soc.*, *77*, 3244 (1955).

is no different in the presence of the ferric chelate of dipivaloylmethane than with the corresponding aluminum chelate. If magnetic field effects, as discussed by Leffler[140], were to play a part in the induced decomposition of RR', one would expect the paramagnetic ferric chelate to have an effect. Since this paramagnetic effect does not occur, the result suggests the examination of less hindered metal chelates would be uncomplicated by such paramagnetic effects for use as inhibitors. Bamford, Jenkins and Johnson[141] have done such experiments in an attempt to count radicals from ABN with ferric chloride.

Finally, the rate of decomposition of RR' in pure styrene, as estimated from the decrease of the rate of polymerization, agrees well with both the results of this work and Trapp's work. A 95 per cent confidence limit places both values within its range of error. The accuracy of this method might be increased by programing a curve fitting analysis of the data on an automatic computer. It is felt that this method for determination of the rate of decomposition is a convenient method, applicable to all initiators in pure monomer. It

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[140] J. E. Leffler, "The Reactive Intermediates of Organic Chemistry", p. 249, Interscience Publishers, Inc., New York (1956).

[141] C. H. Bamford, A. D. Jenkins, and R. Johnson, Nature, (London) 177, 992 (1956).

might suffer complications in very diluted solutions of monomer if the per cent conversion of monomer to polymer were very great.

Estimates of Efficiency of Radical Production for Azo-*Bis*-Isobutyronitrile and Dimethyl-N-(2-Cyano-2-Propyl)-Ketenimine

In the air oxidation study in carbon tetrachloride at 62.5°, the value of 0.64 for the ratio of the efficiency of dimethyl-N-(2-cyano-2-propyl)-ketenimine (RR') to that of azo-*bis*-isobutyronitrile (ABN) is in good agreement with the value of the same ratio which Trapp[142] determined from the rates of polymerization of styrene initiated by the two initiators.

Trapp's work showed[142] that the value of the ratio of the initial rate of formation of RR' to the rate of decomposition of ABN was 0.48 in benzene at 62.5°. Hammond, Sen, and Boozer[143] had earlier established that the efficiency of radical production from ABN was 0.62 under these conditions. These workers also found that the yield of tetramethylsuccinonitrile (RR) in the presence of excess iodine at 80° was 5 per cent. The latter value sets an upper limit on the amount of

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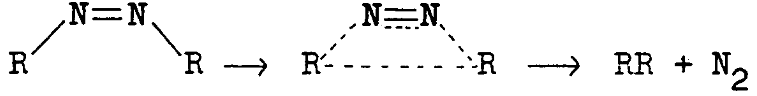
[142] O. D. Trapp, Unpublished Ph.D. Thesis, p. 101, Iowa State College Library, Ames, Iowa (1957).

[143] G. S. Hammond, J. N. Sen, and C. E. Boozer, *J. Am. Chem. Soc.*, *77*, 3244 (1955).

RR which may be produced from the non-oxygen-scavengable initial decomposition of ABN. A material balance of products formed in the decomposition of ABN, using the above information, implies that much more RR' is formed in the non-oxygen-scavengable decomposition of ABN than in the coupling of two "free" cyanopropyl radicals in solution.

This observation supports Trapp's[144] two proposed mechanisms for the decomposition of ABN, one, the non-radical *cis* production of RR', Equation 1, and two, the formation of the azyl radical, Equation 2. The value for the ratio of the efficiency factors of the two initiators is important because it permitted Trapp to argue against the first mechanism on the grounds that to explain the inefficiency of ABN decomposition in this manner would necessarily imply there was little or no cage effect with radicals produced from ABN. The large cage effect observed in the decomposition of RR' is then hard to explain since both decompositions do produce free radicals.

(1)



$$R-N=N-R \longrightarrow R\cdots N{=}N\cdots R \longrightarrow RR + N_2$$

(2) $R-N=N-R \longrightarrow R-N=N\cdot + R\cdot$

The present work indicates that the above value for the ratio of initiator efficiencies from rates of polymerization may be closer to 0.80 than 0.65 because of the lower rate

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[144] O. D. Trapp, *op. cit.*, p. 114.

constant found for the decomposition of RR' in styrene. However, this does not alter the validity of Trapp's argument since the value of the efficiency of RR' determined in the oxidation experiment was 0.32. This value should be compared with a value of 0.50 for ABN. In the case of polymerization, scavenging from the cage by monomer should cause the value for the ratio of efficiency coefficients to approach unity.

In considering rates of polymerization as a method for estimating relative efficiencies of initiators, it should be noted that the data plotted in Figure 2, p. 91 , show that, with the exception of one point at low concentration, RR' obeys the "square-root" relationship, Equation 3, expected for an initiator which decomposes according to first order kinetics in a polymerization system where termination is bimolecular in radical concentration. This relationship has been demonstrated amply for ABN in styrene[145]. This means that the above estimate for relative efficiencies for these two initiators is indeed valid.

$$(3) \qquad R_p = \frac{k_p a^{\frac{1}{2}} k^{\frac{1}{2}} (I)^{\frac{1}{2}} (M)}{k_t^{\frac{1}{2}}}$$

On the other hand, as was noted in the Historical Section of this thesis, there is no general agreement as to the

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[145] C.G. Overberger, F. Fram, and T. Alfrey, Jr., *J. Polymer Sci.*, *6*, 539 (1951).

proper form of the equation for rate of polymerization (Equation 3) as regards the order in monomer concentration. There is agreement that the above equation with first order dependence in monomer concentration does not fit the rate data for solution polymerization of styrene. The value of k_p^2/k_t is not known within a factor of two (since in the evaluation of k_p^2/k_t some value of the rate of initiation and hence of the efficiency, must be assumed) therefore, one cannot directly compare relative efficiencies for a single initiator determined in this manner at different monomer concentrations. (Comparison of efficiencies of two initiators of course are still valid.)

The main suggestions for the general form of the equation for the rate of polymerization will be reviewed briefly. Schulz et al.[146,147] suggest that monomer may form a complex with the initiator and derived Equation 4. Matheson[148] obtained the same equation, with a different interpretation of K, by assuming the monomer could add to caged radicals and that caged radicals recombined to a measurable extent. If one assumes that radicals can diffuse from the cage, one obtains Equation 5. Finally, there is the view taken by Burnett and

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[146] G. V. Schulz and E. Husemann, Z. phys. Chem., B39, 246 (1938).

[147] G. V. Schulz and F. Blaschke, Z. phys. Chem., B51, 75 (1945).

[148] M. S. Matheson, J. Chem. Phys., 13, 584 (1954).

Loan[149] which assumes that alteration of the termination process by radicals derived from chain transfer with solvent takes place. This assumption leads to Equation 6.

$$(4) \quad R_p = \text{Constant x} \left[\frac{K\,(M)\;k\;(I)}{1 + K\;(M)} \right]^{\frac{1}{2}} \quad (M)$$

$$(5) \quad R_p = \text{Constant x} \left[\frac{K' + K(M)}{1 + K' + K(M)} \right]^{\frac{1}{2}} (M)\;k^{\frac{1}{2}}\;(I)^{\frac{1}{2}}$$

$$(6) \quad R_p = \frac{k_p R_i^{\frac{1}{2}}\;(M)}{\left[k_{tmm} + 2k_{tms} \frac{(SH)}{(M)} + k_{tss} \frac{(SH)^2}{(M)^2} \right]^{\frac{1}{2}}}$$

In order to compare the results in this investigation with those of other workers,[145,146,150,151,152] a log - log plot of $C \frac{R_p^2}{(M)^2 k(I)}$ and $C' \frac{R_p}{Mk^{\frac{1}{2}}(I)^{\frac{1}{2}}}$ versus (M) for these data in styrene has been made in Figure 5. Only in the work of this investigation was the rate of decomposition of initiator corrected for

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[149] G. M. Burnett and L. D. Loan, Trans. Faraday Soc., 51, 214, 219 (1955).

[150] F. R. Mayo, R. A. Gregg, and M. S. Matheson, J. Am. Chem. Soc., 73, 1691 (1951).

[151] J. C. Bevington, Trans. Faraday Soc., 51, 1392 (1955).

[152] M. W. Horikx and J. J. Hermans, J. Polymer Sci., 11, 325 (1953).

Figure 5. Comparison of initiated-styrene polymerization rates determined in this investigation with rates from the literature

Ordinate: $C \frac{R_p^2}{(M)^2 k(I)}$ or $C' \frac{R_p}{(M) k^{\frac{1}{2}} (I)^{\frac{1}{2}}}$ (log scale)

Abscissa: monomer concentration (log scale)

△——△ styrene in benzene, $(BzO)_2$[a], 60°[150]; $C' = 2.13 \times 10^5 k^{\frac{1}{2}}$

■— — —■ styrene in benzene, ABN[b], 60°[151]; $C = 6.09 \times 10^6 k$

□—·—□ styrene in toluene, $(BzO)_2$, 50°[c]; $C = 10 \frac{k_t}{k_p}$

⌀-·—·-⌀ styrene in benzene, ABN, 67.9°[145]; $C = 10^{10} k(I)$

-·-·-·- styrene in toluene, $(BzO)_2$, 80°[152]; $C = \frac{k_t}{k_p}$

▲——▲ styrene in benzene, RR'[d], 70°[e]; $C = 10^3$

○——○ styrene in benzene, ABN, 70°[f]; $C = 10^3$

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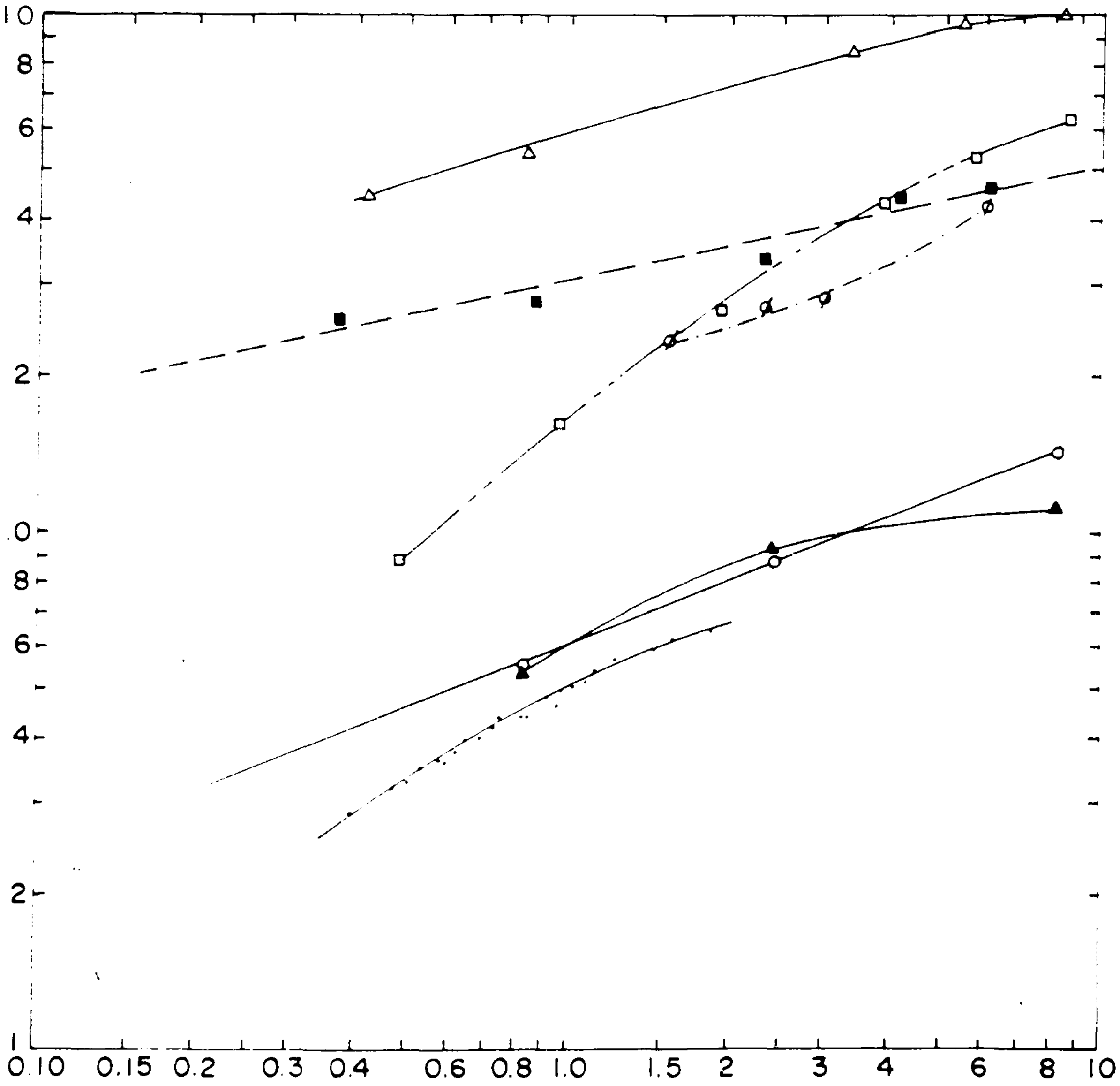
[a] $(BzO)_2$ = benzoyl peroxide.

[b] ABN = azo-bis-isobutyronitrile.

[c] Data from Schulz and Husemann[146] recalculated by Horikx and Hermans[151].

[d] RR' = dimethyl-N-(2-cyano-2-propyl)-ketenimine.

[e] Data from present investigation, Table 5, p. 96.


10
8
6
4
2
1.0
8
6
4
2
1
0.10
0.15
0.2
0.3
0.4
0.6
0.8
1.0
1.5
2
3
4
6
8
10

its dependence on monomer concentration[153]. It may be seen that the ABN data from this investigation agree well with both other benzoyl peroxide and ABN initiated rates in benzene. As was noted before, the variation in rate in toluene solutions differs somewhat from that in benzene.

In the Historical Section of this thesis, arguments against a change of initiator efficiency with monomer concentration were reviewed. However, in the previous subsection, the suggestion was advanced that radical-complexes with monomer could lead to a variation in initiator efficiency with monomer concentration which would not be subject to the earlier criticisms. The increased rate of disappearance of RR' in styrene does suggest such a variation in efficiency with monomer concentration.

On the other hand, Burnett and Loan's study of the rate of polymerization of methyl methacrylate, methyl acrylate, and vinyl acetate in benzene solution certainly suggests alteration of the termination step. In view of the value of 0.62 for the efficiency of ABN as an initiator of air oxida-

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[153] In some work, the product k(I) was not used if all runs were at the same initiator concentration. Thus the positions of the plots and minor variations in the slope are not meaningful in terms of the equations employed. Actually normalization to a similar region on the plot gives little change in slope and for clarity the data were left in the above form. In all cases, the constant C (or C') is tabulated, which shows how the particular data were treated.

tion in benzene[143], one would not expect the efficiency to fall more than one-half in going from pure monomer to low monomer concentrations in benzene. Admittedly at very low concentrations of monomer, the apparent efficiency of radical production could decrease because of termination of growing chains by initiator fragments. Bevington[151] has discussed this possibility. For a 0.015 M solution of styrene, he estimates that termination of growing chains by initiator fragments takes place 33 per cent of the time. However, the estimate is based upon the implicit assumption that cyanopropyl radicals add to styrene no faster than do styryl radicals. This is unlikely to be true. Therefore it is felt that these processes do not play an important part in influencing the rate of polymerization in the concentration ranges involved in this work (greater than 0.01 M monomer) and that Bevington's estimate is grossly high.

Burnett's mechanism of retardation by solvent radicals involved termination of growing chains by phenyl radicals. This seems somewhat unrealistic from two standpoints. Firstly, formation of radicals from benzene and styryl radicals is energetically unfavorable. Secondly, phenyl radicals are sufficiently reactive to make it improbable that they would survive long enough to participate in chain termination.

A significant change in the chemistry of Burnett's mechanism would involve radical complexes with solvent and monomer.

This change retains the logical structure of Burnett's suggestion for the correlation of his polymerization data in the several systems he studied.

For simplicity, let us consider that the initiation step, Equation 7, produces only cyanopropyl radicals, R·, complexed with monomer.

$$(7)\quad 2M + I \longrightarrow \underset{\text{(complex)}}{2M{:}R\cdot} + R\cdot$$

Complexed cyanopropyl radicals, M:R·, will be converted rapidly to complexed monomer radicals, S:M· or M:M·.

$$(8)\quad M{:}R\cdot + S \xrightarrow{k_8} S{:}M\cdot$$

$$(9)\quad M{:}R\cdot + M \xrightarrow{k_9} M{:}M\cdot$$

If these radicals are not produced in an equilibrium distribution, it is reasonable to assume that they will distribute rapidly, Equation 10.

$$(10)\quad S{:}M\cdot + M \overset{K_{eq}}{\rightleftarrows} M{:}M\cdot + S$$

$$(11)\quad K_{eq} = \frac{(M{:}M\cdot)(S)}{(S{:}M\cdot)(M)}$$

Assuming a normal propagation reaction for the two complexed radicals and neglecting monomer consumed in the Steps 8 and 9, the rate of polymerization is given by Equation 12.

$$(12)\quad R_p = k_{pm}(M)(M{:}M\cdot) + k_{ps}(M)(S{:}M\cdot)$$

The elimination of (S:M·) from Equations 11 and 12 gives Equation 13.

$$(13)\quad R_p = \left(k_{pm} + k_{ps}\frac{(S)}{(M)}\frac{1}{K_{eq}}\right)(M)(M{:}M\cdot)$$

Taking into account the three possible termination reactions, the steady state assumption gives Equation 14.

$$(14)\quad R_i = 2k'_{tss}(S{:}M\cdot)^2 + 2k'_{tsm}(S{:}M\cdot)(M{:}M\cdot) + 2k'_{tmm}(M{:}M\cdot)^2$$

Equations 11, 13, and 14 upon elimination of radical concentration give Equation 15 for the rate of polymerization.

$$(15)\quad R_p = \left(k_{pm} + k_{ps}\frac{(S)}{(M)}\frac{1}{K_{eq}}\right)\frac{R_i^{\frac{1}{2}}\,(M)}{2^{\frac{1}{2}}\ k'_{tmm} + k'_{tsm}\frac{(S)}{(M)} + k'_{tss}\frac{(S)^2}{(M)^2}\ ^{\frac{1}{2}}}$$

Equation 13 is very similar in form to Burnett's Equation 6. One notes that no explicit mention need be made of chain transfer, which would take place by a reaction such as Equation 14 where M'_m is unsaturated "dead" polymer.

$$(14)\quad S{:}M_m\cdot + M \longrightarrow M'_m + S{:}M\cdot$$

Actually, Mayo[154] has reported evidence for this type of chain transfer in styrene-bromobenzene solutions. He observed that practically no bromobenzene units are incorporated into

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[154] F. R. Mayo, J. Am. Chem. Soc., 75, 6133 (1953).

the polymer despite the fact that bromobenzene acted as a chain-transfer agent. As has been mentioned earlier, the idea of radical complexes has received experimental support from several other sources. In this case it seems to be a chemically reasonable explanation.

One sees that, if one considers the initiation step, a general equation assuming molecular complexes exceeds in complexity any sort of quantitative treatment of the rather limited amount of data of this investigation.

The values of initiator efficiency divided by inhibitor stoichiometry (computed assuming inhibition is the only process taking place) from Tables 6 and 12 on p. 97 and p. 111, respectively, are plotted versus monomer concentration on a log-log plot in Figure 6. It may be seen that some of these "efficiency values" correlate in an interesting manner to the "efficiency values", $\frac{R_p^2}{k(I)(M)^2}$, calculated from the rate of polymerization. The latter values, as determined in this investigation, are also plotted for comparison in Figure 6. 2,6-Dichloroquinone and 2,5-dichloroquinone both give slopes very similar to the data from rates of polymerization, whereas data from experiments with chloranil give a much steeper slope. It is well established that chloranil copolymerizes with monomers in addition to simply terminating chains. While Table 11, p. 110 shows that the chloranil data

Figure 6. Comparison of initiated polymerization rates with the inhibitor data as a function of monomer concentration in benzene at 70.0°

Ordinate: $\frac{a}{q}$ or $\frac{R_p}{(M)^2 k(I)} \times 10^3$ (log scale)
Abscissa: monomer concentration (log scale)

Polymerization data[a]
▲——▲ RR'[b]
○——○ ABN[c]
Inhibitor data[d]
△- - -△ chloranil, ABN
□- - -□ chloranil, RR'
●-·-● 2,5-dichloroquinone, ABN
■----■ 2,6-dichloroquinone, ABN
ø diphenylpicrylhydrazyl, ABN

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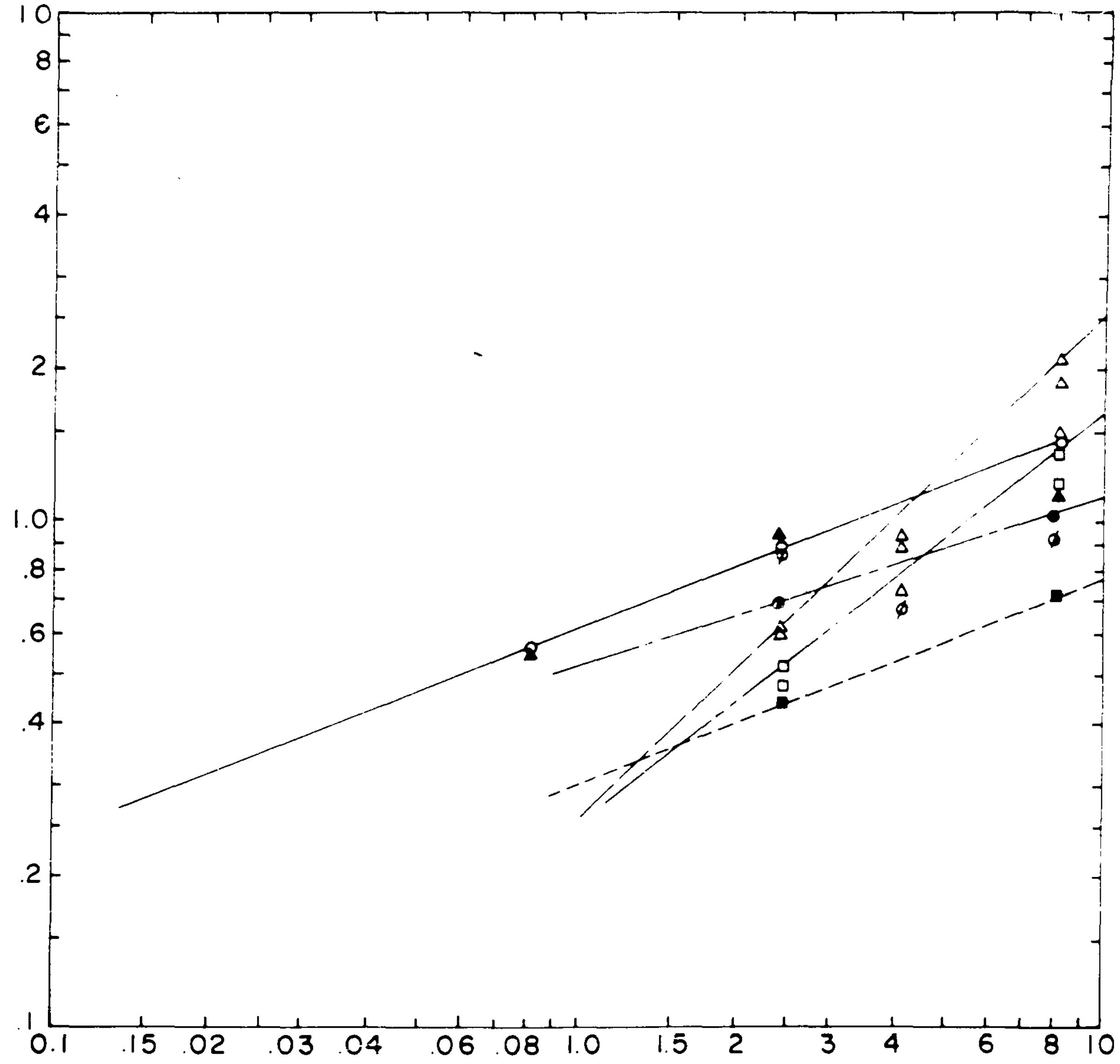
[a] Data from Table 5, p. 96.

[b] RR' = dimethyl-N-(2-cyano-2-propyl)-ketenimine.

[c] ABN = azo-bis-isobutyronitrile.

[d] Data from Table 6, p. 97 and Table 12, p. 111.


10
8
6
4
2
1.0
.8
.6
.4
.2
.1
0.1
.15
.02
.03
.04
.06
.08
1.0
1.5
2
3
4
6
8
10

do not fit the integrated form of a copolymerization equation assuming termination between two chloranil radicals, a consideration of molecular complexes could sensibly affect this equation. The orange color which is obtained when styrene is poured into a yellow solution of chloranil in benzene suggests that chloranil itself forms a complex with styrene. Unpublished measurements by Hammond[155] of ultraviolet and visible extinction coefficients for chloranil in cyclohexane, benzene, and styrene, indicate that chloranil forms complexes with benzene. Using chloranil as a model for chloranil radicals, an interpretation of the above data in terms of molecular complexes does seem reasonable. Since chloranil forms strong charge-transfer complexes, one might expect that radicals derived from the inhibitor would also form such complexes. Other termination mechanisms which were not considered are termination between two styryl radicals and termination between a styryl radical and chloranil radical. The former would not correspond to inhibition. The latter would give a non-linear dependence of the inhibition period on chloranil concentration which is not observed.

Diphenylpicrylhydrazyl (DPPH) data are clearly inconsistent. From Figure 3, p. 101, it can be seen that Runs 68

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[155] G. S. Hammond, unpublished results of work carried out at the University of California at Los Angeles, (1948). Present address: Chemistry Dept., Iowa State College, Ames, Iowa.

and 75 gave fairly well defined induction periods which are in good agreement with the time of disappearance of the characteristic purple color of DPPH. Run 67 on the other hand did not give a well-defined induction period and the time of the color change (which was also not clearly defined) was used to calculate the ratio of the efficiency factor to inhibitor stoichiometry. If Run 67 is disregarded, the DPPH data agree well with the data from the two dichloroquinones. This result would be expected from Kice's work[156, 157] which demonstrates that these two quinones copolymerize only to a very small extent with vinyl acetate and methyl methacrylate. The evidence implying that initiator efficiencies vary with monomer concentration would fit with the explanation of the increased rate of disappearance of RR' in styrene discussed in the previous section.

The study of inhibition periods yields conclusions concerning initiator efficiencies which are nearly sufficient to explain the variation in the rates of uninhibited polymerization. Therefore, there is little evidence for any significant solvent effects on the rates of chain termination in the absence of inhibitors in this concentration range. Such a result contrasts with earlier observations with solution poly-

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[156] J. L. Kice, J. Am. Chem. Soc., 76, 6274 (1954).

[157] J. L. Kice, J. Polymer Sci., 19, 123 (1956).

merization of vinyl acetate, methyl acrylate, and methyl methacrylate. That styryl radicals should be less sensitive to medium effects in benzene-styrene mixtures is consistent with the differences in electronic character usually assigned to the various radicals.

However, should Run 67 prove to be correct, the interpretation would not be as clear. While solvent termination could be invoked as an explanation for the changes in rate of polymerization, one would still have to explain the large amount of copolymerization taking place with the dichloroquinones as well as the increased rate constant for disappearance of RR'. Such a result would fit both with Bevington's view and his data on isolation of RR in styrene-benzene solutions. However, the infrared measurements of initial rate of formation of RR' in styrene, Table 23, p. 145, do not agree with these data. It is felt that these latter measurements would, if anything, overestimate the production of RR' since the temperature of such a solution at high initiator concentration would be somewhat higher than the temperature of the bath and since ketenimine linkages incorporated into the polymer would count as RR'.

Finally, the results of the inhibition of the thermal polymerization should be noted. One can see from Table 14, p. 114, that chloranil and DPPH are consumed 10 and 85 times more rapidly than would be expected from comparison of the rates of thermal and initiated polymerization. The stoichiometries determined for chloranil are affected less than one per cent and those determined for DPPH may be in error by five per cent, because of the thermal reaction between monomer and inhibitor.

In conclusion it may be said that further work is indicated. From the experiments of Bamford[158] and coworkers using ferric chloride as an inhibitor in a dimethylformamide solution of styrene, it can be seen that an oil soluble analogue of ferric chloride would be ideal for determination of the variation of initiator efficiency. The ferric chelate of dipivaloyl methane, while oil soluble as is evidenced by Run 73, is too unreactive to serve as an inhibitor. Perhaps a diester of hemin would be a better possibility to try in future work. Even if such an ideal inhibitor is unavailable, the present study should be extended to include an analysis of the extent of copolymerization using Kice's development[156, 157]. Also, in view of the heating problems involved, redesigned dilatometers would improve the precision of measurement of the rates of polymerization. Although the data are preliminary, the complications encountered in this study point to a more detailed understanding of free-radical polymerization processes.

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[158] C. H. Bamford, A. D. Jenkins, and R. Johnson, Nature (London), 177, 992 (1956).

SUMMARY

Several independent experiments indicate that the efficiency of radical production from the initiators, azo-bis-isobutyronitrile (ABN) and dimethyl-N-(2-cyano-2-propyl)-ketenimine (RR'), varies with monomer concentration in styrene polymerization. The salient observations about the experiments which support the above assertion are as follows:

1. The ratio of the initiator efficiency factor to the stoichiometric factor for inhibition, a/q, as measured from inhibition periods decreases with decreasing monomer concentration. The effect of inhibitor-monomer copolymerization is neglected in the calculation of a/q.

2. The initiator efficiency, a, as calculated from the rate of polymerization varies with monomer concentration in a manner quite similar to the variation of a/q calculated for two dichloro-substituted quinones which are believed not to copolymerize appreciably. While the variation of the a calculated in this manner is considerably less than the variation of a/q found for chloranil, it is known that this quinone does copolymerize with monomer.

3. The ratio of the rates of polymerization of ABN and RR' in styrene indicate that the ratio of their efficiency factors is 0.80 rather than 0.64 as found in air oxidation experiments in which no monomer is present.

4. The initial fraction of ABN which goes to RR' upon decomposition of ABN is considerably lower in styrene than in benzene.

5. Trapp's observation that the rate of decomposition of RR' increases considerably with monomer concentration was checked both directly by quantitative infrared measurements and indirectly by the form of the decrease in the rate of polymerization due to decomposition of initiator.

A proposal is advanced that monomer may complex with radicals from the decomposition of the initiator thereby decreasing the importance of cage effects.

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