SOLUTION-DECOMPOSITION AND POLYMERIZATION-INITIATOR ACTIVITY OF DIAZO-THIO-ETHERS

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Ernest W. Cotten

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INTRODUCTION

In connection with a war-project sponsored by the Office of Rubber Reserve, Reconstruction Finance Corporation, the use of diazo-thio-ethers, R-N=N-S-R', as initiators and modifiers in emulsion polymerization was reported in June, 1944[1]. Initiators are usually defined as compounds furnishing molecules or radicals of high energy-content, which are capable of initiating the growth of long-chain molecules of the monomers, or substances to be polymerized. Modifiers are substances capable of reacting with the growing polymer chains, causing a termination of their growth and thus modifying the molecular-weight of the final polymer.

Study of the structure of the copolymer of butadiene and styrene indicates it to be a mixture of alternate units consisting of one or several styrene molecules joined by 1,4- and 1,2- addition to one or several butadiene molecules, long chains being formed in this manner. From study of the kinetics and general characteristics of this reaction it is well-established that the formation of rubbery or high-molecular-weight polymers is the result of a chain reaction. Chain reactions are generally defined as those wherein the activation of a single molecule may cause a series of successive reactions to take place, until

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[1] Reynolds, W. B.: Diazo-thio-ethers as Catalyst-Modifiers. Rubber Reserve Co. technical report No. CR-408 from University of Cincinnati, June, 1944.

a large number of molecules has been transformed. Such reactions may be catalyzed by a wide variety of substances, according to Christiansen and Kramers[2]. Such an activated molecule may be a molecule of the monomer-mixture activated through collision with--and consequent absorption of energy from--another molecule, or it may be a molecule of another substance entirely, which has acquired its energy by means of some other mechanism, e. g., through some reaction which leaves it with a high energy-content and consequent high reactivity.

In emulsion polymerization of styrene and butadiene, standard practice has been to use a combination of a mercaptan and an oxidizing agent, the oxidant functioning to produce free radicals of the type MS· by reaction with the mercaptan. These free radicals then serve as the activated centers mentioned before, reacting with monomer molecules to produce chains, as follows:

$$\mathrm{MS\cdot + Ph{-}CH{=}CH_2 \;=\; Ph{-}\underset{\bullet}{C}H{-}CH_2SM}$$

$$\mathrm{Ph{-}\underset{\bullet}{C}H{-}CH_2SM + CH_2{=}CH{-}CH{=}CH_2 \;=\; Ph{-}CH(CH_2SM)CH_2CH{=}CH\underset{\bullet}{C}H_2}$$

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Finally, the chains are terminated by reaction with unattacked mercaptan, the modification process being postulated as follows:

$$\mathrm{R\underset{\bullet}{C}H_2 + MSH \;=\; RCH_3 + MS\cdot}$$

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[2] Christiansen and Kramers: J. Chem. Soc. <u>126</u>, (2), 28 (1924)

More free radicals are thus produced which in turn may propagate new chains until the supply of monomer is used up. In the standard formula, use is made of a water-soluble oxidizing agent, potassium persulfate, and an oil-soluble normal mercaptan mixture which has an average molecular weight corresponding to a content of twelve carbon atoms, or $C_{12}H_{25}SH$. An emulsifying agent, SF-flakes, consisting of a mixture of soaps of long-chain acids such as oleic and palmetic, together with shorter-chain acids like lauric, is used in the standard formula. It is postulated that the water-soluble oxidizing agent reacts with the mercaptan dissolved in the monomer mixture to produce free radicals, $C_{12}H_{25}S^{*}$, which initiate the chains of polymer. The locus of reaction at low conversions is thought to be the micelle, which is an aggregate, complicated in structure, of molecules of the emulsifier, and which serves to dissolve small but significant amounts of the monomers in the aqueous phase. After growth of the chains, they are terminated by reaction with unattacked mercaptan, which thus acts as the modifier. For bulk-polymerizations, as opposed to those taking place in an emulsion, oil-soluble catalysts must be used.

Certain disadvantages inherent to the standard persulfate-mercaptan combination have become apparent in work on synthetic rubber. The persulfate enters into undesirable side-reactions, and the mercaptan is consumed out of all proportion to its function as part of the promoter system or as modifier. Attempts to overcome these defects have been made, for example, by adding the mercaptan in increments, or by use of a system where mercaptan is produced throughout the course of the reaction.

Diazoamino compounds have been used previously to catalyze polymerization reactions. Thermal decomposition of these compounds results in formation of free radicals which promote the polymerization. The chief disadvantage of this type of catalyst is that it does not function as a modifier, and also a fairly large quantity is required to obtain satisfactory reaction rates.

Diazo-thio-ethers in emulsion polymerizations have been the subject of a good deal of investigation since 1944, since they appear to possess appreciable commercial significance. In explaining their function as polymerization initiators it has been assumed that an aromatic free radical and a mercaptan free radical are products of the thermal decomposition:

$$R\text{-}N{=}N\text{-}S\text{-}R' \ = \ R\cdot + R'S\cdot + N_2$$

If this hypothesis is correct, then chain-initiation and modification may both be explained by several possibilities, to be taken up later.

HISTORICAL BACKGROUND

A number of diazo-thio-ethers are described in the literature though no reference to their use as polymerization catalysts or modifiers before 1944 could be found.

In 1866, Griess[3], in an attempt to make thiophenol by Leuckart's reaction, treated benzene diazonium chloride with K_2S. He obtained an explosive oil that did not prove to be thiophenol, hence the investigation was not carried further. This is similar to the work of Klason[4] in 1887.

Graebe and Mann[5], in 1882, were looking for a convenient method of synthesis for diphenyl sulfide. They treated benzene diazonium salt with H_2S or ammonium sulfide. On decomposition of the resulting compound in water, they obtained diphenyl sulfide and diphenyl disulfide. The experiment was repeated using toluidine and alpha- and beta-naphthylamines, but the decomposition products in the latter cases were not identified.

In 1884, Stadler[6] made and identified the first diazothio-ether in an attempt to find a method for identification of mercaptans. He hoped to be able to form the azothiol derivatives by analogy with azo-hydroxy compounds. He reacted diazotized sulfanilic acid in the cold with ethyl mercaptan, in the presence of caustic. Existence of the nitrogen-sulfur bond was proved by analysis of the resulting compound, the sodium salt, for sodium. By showing only one sodium atom present per molecule, the structure $NaO_3S\text{-}C_6H_4\text{-}N{=}N\text{-}S\text{-}C_2H_5$, instead of $NaO_3S\text{-}N{=}N\text{-}C_2H_4\text{-}SNa$, was

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[3] P. Griess: Ann. 137, 74 (1866)
[4] P. Klason: Ber. 20, 349 (1887)
[5] Graebe and Mann: Ber. 15, 1683 (1882)
[6] Stadler: Ber. 17, 2095-81 (1884)

shown to be preferable. He also prepared the diazo-thioether from aniline and ethyl mercaptan, and decomposed it in ether solution by heating. Phenyl-ethyl sulfide and diethyl disulfide were identified from the decomposition products.

Leuckart[7], in 1889, treated thio-2-naphthol with diazotized sulfanilic acid in cold, strongly alkaline solution. He believed his product to be the azo-thiol compound, in the form of the sodium salt. The solution of the salt was acidified and heated. Nitrogen was produced, besides thio-2-naphthol and the sodium salt of phenol sulfonic acid.

In 1890, Ziegler[8]prepared several sulfides, all from thiophenol. He was interested in developing a method for synthesis of substituted mixed sulfides, by decomposition of the diazo-thio-ethers. The diazonium solution was added slowly to an alkaline solution of thiophenol at 60-70°C. In this manner he succeeded in making sulfides from thiophenol and the following aromatic amines: aniline, p-toluidine, alpha- and beta-naphthylamines, p-aminoacetanilide, and anthranilic acid. Since the diazo-thio-ethers formed were decomposed immediately by the temperature of coupling, only the thio-ethers, or sulfides, were reported.

Graebe and Schultess[9], in 1891, made thioxanthone by

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7. Leuckart: J. Prakt. Chem. (2) <u>41</u>, 220 (1889)
8. Ziegler: Ber. <u>23</u>, 2469-72 (1890)
9. Graebe and Schultess: Ann. <u>263</u>, 1-15 (1891)

use of a diazo-thio-ether from anthranilic acid and thiophenol. This was decomposed to phenyl-thiosalicylic acid by heating, and the latter converted to thioxanthone by dehydration.

In 1894, Jacobson[10] made the most stable diazo-thio-ether reported in the literature. He diazotized o-amino-thiophenol, made the mixture alkaline, and filtered off a product which proved to be benzo-thio-(a,b)diazole. A cryoscopic molecular weight proved slightly higher than that represented by the formula. This compound was stated to be stable under 175°C., though Hantzsch later[11] reported 163°C., and was purified by vacuum distillation. It forms addition compounds with heavy-metal halides and alkyl halides of low molecular weight. By decomposition at 200-250°C., Jacobson was able to isolate a cyclic sulfide. Hantzsch[11], later in 1909, used the same diazo-thio-ether for a study of the effect of structure on color.

Perhaps the most comprehensive early work on the diazo-thio-ethers was done in 1895 by Hantzsch and Freese[12]. They hoped to be able to gain information on the stereoisomerism of azo-compounds by a study of the diazo-thio-ethers. A number of the latter were prepared from thiophenol, using the bases following: aniline, p-chloraniline, p-bromaniline, p-iodoaniline, 2,4-dichloraniline, 2,4-dibromaniline, 2,4-diiodoaniline, 2,4,6-tribromaniline, p-nitraniline, and sul-

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[10] Jacobson: Ann. 277, 219 (1894)
[11] Hantzsch: Ber. 42, 68-85 (1909)
[12] Hantzsch and Freese: Ber. 28, 3237 (1895)

fanilic acid. The compounds were purified by dissolving in absolute ether and passing in anhydrous hydrogen chloride to complete precipitation of the addition product. This was filtered off and pumped dry in a vacuum desiccator, the HCl being spontaneously eliminated, leaving the pure diazo-thio-ether. Several of the compounds were decomposed in water or alcohol and the decomposition products identified. When decomposed in aqueous solution or suspension, the diazo-thio-ethers were observed to give, in addition to the mixed sulfide formed by simple elimination of nitrogen, substantial quantities of the disulfide of the mercaptan from which the original compound had been formed, i. e., diphenyl disulfide. They believed that this might be due to hydrolysis of the diazo-thio-ether to the diazonium compound and the mercaptan, with subsequent air-oxidation of the mercaptan to the disulfide. Evidence of phenolic compounds was found, substantiating the theory of the formation of diazonium salts and their subsequent decomposition in the presence of water. However, they also observed the disulfide to be formed when the decomposition of the diazo-thio-ether was allowed to take place in absolute alcohol. Consequently the disulfide must be regarded as a prime product of decomposition, since these authors reported a 39 percent yield of diphenyl disulfide from decomposition in water of the sodium salt of the diazo-thio-ether from sulfanilic acid and thiophenol.

In 1896, Bamberger and Kraus[13] investigated a series of compounds which they designated as the diazo-hydrosulfides. The following compounds were prepared from p-nitroaniline diazo and hydrogen sulfide: $NO_2-C_6H_4-N=N-SH\cdot H_2S$, $(NO_2-C_6H_4-N=N-S-)_2$, and $NO_2-C_6H_4-N=N-S-N=N-C_6H_4-NO_2$. The last compound was highly explosive, even in water. Investigation of the effects of aromatic solvents on di-(p-nitrophenyldiazo-) disulfide, which was not explosive, led to the identification of substituted biphenyls and substituted disulfides. For example, benzene and the diazodisulfide gave p-nitrobiphenyl and p,p'-dinitrodiphenyl disulfide, together with elementary sulfur. In the same year, Bamberger[14] reported the preparation of the diazo-thio-ether from p-chloraniline and thiophenol, though the compound possessed a considerably higher melting-point than that reported earlier by Hantzsch and Freese.

In 1906, Friedlaender[15] used the diazo-thio-ethers for preparation of arylthioglycollic acids, to be used in synthesis of sulfur analogs of indigo. He coupled p-nitroaniline to thioacetic acid, but was unable to isolate the desired sulfide on decomposition. When aromatic amines were coupled to thioglycollic acid, the formation of the diazo-thio-ethers and subsequently of the sulfides was said to be smooth and easy. It might be mentioned that this work could not be repeated by the present authors,

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[13] Bamberger and Kraus: Ber. 29, 272 (1896)

[14] Bamberger: Ber. 29, 468 (1896)

[15] Friedlaender: Ber. 39, 1060 (1906)

using the procedure as given. In another paper of the same year, Friedlaender[16] reported the preparation of the diazo-thio-ether from anthranilic acid and thioglycollic acid. This was decomposed in water, ethyl acetate, acetone and nitrobenzene. In all cases substantial amounts of the o-carboxyphenyl thioglycollic acid were reported. In another paper in 1907, preparation of diazo-thio-ethers from thioglycollic acid and the following amines were reported by Friedlaender and Chwala[17]: p-bromaniline, p-nitraniline, p-toluidine, 2-naphthylamine, o-phenylenediamine, m-chloraniline, and alpha-aminoanthraquinone. From thioacetic acid, diazo-thio-ethers were made from p-nitraniline and p-bromaniline. In the following year several German patents were issued to Kalle and Company[18], covering the synthesis of arylthioglycollic acids by decomposition of the corresponding diazo-thio-ethers in water, alkali, or inert solvents.

Fox and Pope[19], in 1912, were interested in the sulfur analog of benzene-azo-phenol. Small amounts of p-nitrobenzene-azo-phenyl methyl mercaptol were obtained, after methylating a product of the reaction between p-nitraniline diazo and thiophenol. However, they state that by far the main product was 2-(p-nitrobenzene-diazo-mercapto-) benzene, as was to be expected from the work of Hantzsch and Freese.

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16. Friedlaender: Ann. 351, 390-420 (1906)
17. Friedlaender and Chwala: Monatsh. 28, 247 (1907)
18. Kalle and Co.: Chem. Zentr. I, 1221 (1908); ibid. II, 1070 (1908)
19. Fox and Pope: J. Chem. Soc. 101, 1498 (1912)

Vorlander and Mittag[20], working with triphenylmethyl sulfur compounds in 1919, added aqueous benzene diazonium chloride to a saturated cold alcoholic solution of triphenylmethyl thiocarbinol. On making the mixture alkaline, the diazo-thio-ether precipitated. It was insoluble in fairly strong caustic, showing the mercapto-group to be bound as a result of the reaction.

In 1928, Finzi[21], being interested in linear dithioxanthones, used a bifunctional mercaptan, meta-dimercaptobenzene. Two moles of the following bases were coupled to it in each case: anthranilic acid, o-aminobenzyl alcohol, and alpha-carboxy-beta-naphthylamine.

Pollak and Gebauer-Fulnegg[22], in 1928, used the same mercaptan and two moles of sulfanilic diazo. They also reacted two moles of p-nitraniline diazo with 1,5-dimercaptonaphthalene, 2,4-dimercaptophenol, and 2,4-dimercapto-5-methyl phenol, in addition to coupling p-nitraniline to thio-beta-naphthol. They were interested in the tinctorial properties of the compounds. Consequently their technique was to pad cotton with an alkaline thiol or dithiol, subsequently developing with a diazo. The compounds were found to be useless as dyes since they decompose at the temperature of boiling water.

In 1934, Dunn and Fletcher[23] prepared several diazo-

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[20] Vorlander and Mittag: Ber. 52, 423 (1919)
[21] Finzi: Gazz. chim. ital. 58, 269 (1928)
[22] Pollak and Gebauer-Fulnegg: Monatsh. 50, 310 (1928)
[23] Dunn and Fletcher: Trans. Kansas Acad. Sci. 37, 123 (1934)

thio-ethers from thio-beta-naphthol. Bases used were aniline, m-toluidine, beta-naphthylamine, sulfanilic acid, and 1-naphthylamine-4-sulfonic acid. Sulfanilic acid was also coupled to p-thiocresol. These diazo-thio-ethers were all solids, in contrast to the unworkable oils obtained from some mercaptans.

USE OF DIAZO-THIO-ETHERS AS CATALYSTS OR CATALYST-MODIFIERS IN EMULSION POLYMERIZATIONS

The use of diazo-thio-ethers as emulsion polymerization initiators and modifiers was reported by this laboratory to the Polymer Research Branch of the Research and Development Section of the Office of Rubber Reserve in June, 1944, in technical report No. CR-408[1]. In that paper the synthesis and evaluation of a series of diazo-thio-ethers of the type R-N=N-S-R' are described. Since the rate of thermal decomposition of the compounds seemed to depend primarily on the electronegativity of the radicals R and R', a systematic approach to the problem was made by synthesizing approximately thirty-five diazo-thio-ethers, using radicals of varying electronegativity for R and R' by choice of suitable bases and mercaptans. In this way, the effects of varying the electronegativity of R and R' were observed with respect to catalyst- and modifier-activity. Each product was evaluated in Type I formula, substituting 0.01 mole-parts of the diazo-thio-ether for the persulfate-mercaptan system. Type I formula is as follows:

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[1] loc. cit.

Soap, 5 parts; persulfate, 0.3 parts; mercaptan, 0.5 parts; water, 180 parts; butadiene, 72 parts; styrene, 28 parts. Polymerization rates were followed by observing the volume change in sealed tubes, according to the Fryling[24] technique. Modifier activity was estimated from benzene solubility of coagulated rubber.

In addition, the preparation and evaluation of eight water-soluble (containing a water-solubilizing group on either or both radicals R and R') diazo-thio-ethers is reported in January, 1945, technical report No. CR-591[25]. These compounds were, in addition to the modified Type I formula, evaluated in a similar recipe where the soap used as emulsifier was replaced by a non-micellular (non-solubilizing) emulsifier, such as Aerosol AY, which is a sulfonated di-cyclohexyl succinate. The effects of pH and of lower polymerization temperature were noted. It was observed that the effect of water-solubilizing groups is to increase greatly the rate of thermal decomposition in solution and hence the catalytic activity. At 50°C., there was a tendency to obtain very rapid polymerization rates for a short time with the reaction stopping at relatively low conversion.

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24. Fryling: Ind. Eng. Chem., Anal. Ed. 16, 1 (1944)
25. Reynolds et al.: Water-Soluble Diazo-thio-ethers as Catalyst-Modifiers. Rubber Reserve Co. technical report No. CR-591, from University of Cincinnati, January, 1945

In report number CR-610[26], in March 1945, are reported the results of five-gallon reactor polymerizations using, respectively, the diazo-thio-ethers from p-anisidine and thio-2-naphthol, and from sulfanilic acid and p-thiocresol (in the form of the sodium salt). Also reported are charges made according to the Kolthoff and Dale[27] recipe, which uses Sulfole (a mixture of tertiary C_{14} mercaptans), potassium ferricyanide, and the diazo-thio-ether from p-anisidine and thio-2-naphthol, designated as "MDN". New diazo-thio-ethers from 3-aminopyridine and 5-aminoquinoline with thio-2-naphthol are reported. Evaluation of these two compounds is reported in CR-638[28], in April, 1945, as well as synthesis and evaluation of 5-aminoquinoline coupled to thiosalicylic acid.

In Report CR-697[29], the synthesis of three new diazo-thio-ethers, using "Captax" (2-mercaptobenzothiazole), is reported. Bases used were p-anisidine, p-chloraniline, and sulfanilic acid. Evaluation as catalyst-modifiers was also reported.

Preparation and evaluation as initiators of two diazo-thio-ethers, namely from p-aminobenzoic acid and 2-mercaptobenzothiazole, and from p-aminobenzoic acid and p-thio-

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[26] Reynolds: Progress Report for February, 1945. Rubber Reserve Co. technical report No. CR-610, from University of Cincinnati, March, 1945.

[27] Kolthoff and Dale: MDN as Activator-Modifier in Polymerizations by Various Recipes. Rubber Reserve Co. technical report No. CR-522, from University of Minnesota, 1944.

[28] Reynolds: Progress Report for March, 1945. Rubber Reserve Co. technical report CR-638; University of Cincinnati, April, 1945.

[29] Reynolds: Progress Report for April, 1945. Rubber Reserve Co. report CR-697; University of Cincinnati, 1945.

cresol, is reported in CR-729[30].

Controlled increment addition of 2-(p-methoxybenzene-diazo-mercapto)-naphthalene (MDN) to a polymerization run is reported in CR-763[31]. Increment addition was tried as a means of avoiding over-modification near the beginning of the reaction, when the concentration of the diazo-thio-ether was high, and under-modification near the end of the reaction, when much of the diazo-thio-ether present had decomposed thermally. It was hoped to be able to obtain a constant-viscosity rubber in this way, viscosity being a function of average molecular weight of the polymer. Rate of reaction was unaffected by increment addition, but final conversion value proved higher than usually obtained by orthodox methods. New diazo-thio-ethers prepared and evaluated as catalysts were: ortho-anisidine to thio-2-naphthol, 2,5-dimethoxyaniline to thio-2-naphthol, 2,5-dimethoxyaniline to p-thiocresol, p-anisidine to p-thiocresol, and 2,5-dimethoxyaniline to thiosalicylic acid. In this report it was noted that ortho-substituted bases gave compounds of considerably less activity than did the isomeric para-substituted bases, even though in the electronegativity series the two may occupy approximately equal levels.

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30. Reynolds: Progress Report for May, 1945. Rubber Reserve Co. technical report No. CR-729, from University of Cincinnati, June, 1945.

31. Reynolds: Progress Report for June, 1945. Rubber Reserve Co. technical report No. CR-763, from University of Cincinnati, July, 1945.

In Report No. CR-821[32], the following new diazo-thioethers were prepared and evaluated: p-aminoacetanilide to thio-2-naphthol, 2-naphthylamine to p-anisyl mercaptan, p-anisidine to p-anisyl mercaptan, p-aminophenyl acetic acid to thio-2-naphthol, and 2,4-dimethylaniline to thio-2-naphthol. Prepared by a slightly different technique, namely coupling in glacial acetic acid in the presence of sodium acetate, due to the low solubility of the mercaptans in caustic solution, were several diazo-thio-ethers from aliphatic mercaptans. Those prepared and evaluated were: p-nitraniline to t-butyl mercaptan, and p-chloraniline coupled to, respectively, t-butyl, t-octyl, and t-dodecyl mercaptans. Compounds from aliphatic thiols were more active than those from aromatic mercaptans. The higher the molecular weight of the tertiary aliphatic mercaptans tried, the more active was the diazo-thio-ether as a catalyst.

It should be mentioned that earlier, in CR-468[33], it had been noticed that bottle polymerizations are more rapid and give better-modified rubber than tube polymerizations, when diazo-thio-ethers are used in place of the persulfate-mercaptan system. This results, probably, from better agitation. However, for purposes of preliminary evaluation, tube polymerizations afforded a convenient and a more rapid

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[32] Reynolds: Progress Report for Sept.-Nov., 1945 Rubber Reserve Co. technical report No. CR-919, from University of Cincinnati, November, 1945.

[33] Reynolds: Progress Report for October, 1944. Rubber Reserve Co. technical report No. CR-468, from University of Cincinnati, November, 1944.

means of comparison of different diazo-thio-ethers than did bottle polymerizations.

PRESENT INVESTIGATION

A. Scope and General Method

The present investigation was undertaken with the objective of learning more about the chemistry of the diazo-thio-ethers and the mechanism by which they function as initiators and modifiers.

Qualitatively, the activities of the diazo-thio-ethers as polymerization initiators seemed to be related to their solution-instability on heating. Those compounds which evolve nitrogen rapidly in solution seemed to be the most active initiators. This was assumed to be due to the high concentration of free radicals available for the purpose of initiating chains. Also, it had been observed that diazo-thio-ethers containing activating substituents, such as alkyl- and alkoxyl-, in either the diazo or the mercaptan part of the molecule, give unstable solutions and are the most active initiators. Those that contain deactivating substituents, e. g., chloro- and nitro-, give much more stable solutions and are the least active initiators. Furthermore, it was observed that all diazo-thio-ethers are much more stable in solution in non-polar solvents than they are in solution in polar solvents.

In view of these observed qualitative relationships, it was decided to determine quantitatively to what extent solution decomposition rates could be correlated with initiator activity and also with the electronegativities of the diazo-radicals. Electronegativity is used in the sense proposed by Kharasch and coworkers[34], and is defined as the relative ease with which, in unsymmetrical organo-mercury compounds, the bond between the radical and mercury is split by hydrogen chloride to give the corresponding hydrocarbons.

In explaining the function of the diazo-thio-ethers as initiators in polymerizations, it has been assumed that an aromatic free-radical and a mercaptan radical are products of the thermal decomposition:

$$R{-}N{=}N{-}S{-}R' \;=\; R\cdot + R'{-}S\cdot + N_2$$

If this hypothesis is correct, then chain-initiation might be caused by one or more of the following four possibilities:

A. Mercaptan Radical:

1. $R'{-}S\cdot + M \;=\; R'{-}S{-}M\cdot$
2. $R'{-}S\cdot + M \;=\; R'{-}SH + M'\cdot$
   ($M'\cdot$ equals M less $H\cdot$)

B. Aromatic Radical:

3. $R\cdot + M \;=\; R{-}M\cdot$
4. $R\cdot + M \;=\; RH + M'\cdot$

Reaction (1), combination of a mercaptan radical with a monomer molecule to give an activated adjunct, is the familiar step usually given for the initiation of the polymer

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[34] Kharasch and Marker: J. Am. Chem. Soc. 48, 3130 (1926); Kharasch and Flenner: ibid. 54, 674 (1932); Kharasch, Reinmuth and Mayo: J. Chem. Ed. 11, 82 (1934); ibid. 13, 7 (1936)

chain in the mercaptan-persulfate emulsion system. On the basis of previous evidence, however, it would seem that reaction (2), where a mercaptan radical strips hydrogen from a monomer molecule to give an activated monomer radical, represents an equally logical possibility, since the sulfur content of the polymer could be introduced in the termination step equally as well as in the initiation step. For example, a mercaptan radical could react with a growing chain. Argument that chains may be both initiated and terminated in a variety of ways does not impose on the limitation, set by observation, that the sulfur-content of the polymer is, roughly, inversely proportional to its molecular weight.

Aromatic free-radicals are extremely reactive in organic solutions, as shown by Kharasch and coworkers[34]. This fact would seem to indicate that they might not be expected to add to a monomer molecule according to reaction (3) above. There is ample evidence that they can easily extract an aliphatic hydrogen atom from a solvent. Consequently, it would be a logical inclination to favor reaction (4) as the mechanism by which the aromatic radical from the diazo-thio-ether is able to initiate chains.

In order to elucidate the possible mechanism of the chain-initiation step, it was deemed advisable to study the solution-decomposition products of a diazo-thio-ether, since the literature gives little evidence of a thorough investigation of this type. According to the literature, the chief products of decomposition were those resulting from hydrolysis or simple nitrogen elimination:

$$2\ \mathrm{R{-}N{=}N{-}S{-}R'} + 2\ \mathrm{HOH} = 2\ \mathrm{ROH} + 2\ \mathrm{R'SH} + 2\ \mathrm{N_2}$$

(Disulfide formation) $2\ \mathrm{R'SH} \overset{(O)}{\underset{\mathrm{air}}{=}} \mathrm{R'S{-}SR'} + \mathrm{H_2O}$

(Mixed-sulfide formation) $\mathrm{R{-}N{=}N{-}S{-}R'} = \mathrm{R{-}S{-}R'} + \mathrm{N_2}$

Little information was obtainable concerning the products of decomposition in an anhydrous solvent, other than the fact that mixed sulfide and disulfide had been identified.

For the decomposition-products study, anhydrous tetralin, or 1,2,3,4-tetrahydronaphthalene, was chosen as solvent, since it combines aromaticity with a capacity to donate hydrogen atoms. 2-(benzene-diazo-mercapto)-naphthalene was chosen as the diazo-thio-ether on the indication that its decomposition products might be easily identified by comparison with the literature.

B. Summary and Discussion of Results

1. Introduction

Kharasch and coworkers[34] have developed a table of relative "electronegativities" based upon the relative ease of splitting organo-mercury compounds with hydrogen chloride. There seems little doubt that the electronegativity series represents a classification that carries over into a great variety of correlations between structure and chemical reactivity. Consequently, it was deemed of interest to see to what extent electronegativities

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[34] *loc. cit.*

correlate with the polymerization rates and the solution-decomposition rates observed for the diazo-thio-ethers.

Tiffeneau[35] originally discussed a property of organic radicals which he termed "migratory aptitude". If there is equal opportunity for two different radicals to migrate in a chemical rearrangement, the one which preferentially migrates is said to have a higher "migratory aptitude". By study of the pinacol-pinacolone rearrangement, Bailar[36] and Bachmann and coworkers[37] have extended the work of Tiffeneau and assigned quantitative values for migratory aptitude, as follows: p-anisyl (500), 1-naphthyl (18), p-tolyl (15.7), 2-naphthyl (greater than 1), phenyl (1), p-chlorophenyl (0.66), o-anisyl (0.3), o-chlorophenyl (very small). In the rearrangement studied, aromatic groups with ortho-substituents migrate with great difficulty, possibly because of steric influences. Hence the method is not reliable for ortho-substituted groups, but otherwise the agreement with the electronegativity series is close.

Hixon and Johns[38] discussed the basicity of primary aromatic amines and listed the relative values of the dissociation constants, based on a value of 3×10^{-10} for phenyl, in decreasing order as follows: p-anisyl (20), p-tolyl (6.7), o-tolyl (1), phenyl (1), o-anisyl (0.67),

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35. Tiffeneau: Bull. soc. chim. 35, 1639 (1924)
36. Bailar: J. Am. Chem. Soc. 52, 3596 (1930)
37. Bachmann et al.: J. Am. Chem. Soc. 54, 1132 (1932); ibid. 56, 2081 (1934)
38. Hixon and Johns: J. Am. Chem. Soc. 49, 1786 (1927)

1-naphthyl (0.3), p-chlorophenyl (0.033), p-nitrophenyl (0.0033), and o-chlorophenyl (0.0030). It may be noticed that ortho-substituted groups are not in line with the electronegativity series in this classification either, but with this exception the agreement is fairly good, qualitatively speaking.

2. Correlation between Electronegativities and Solution Decomposition Rates

In the following table the electronegativity series is compared with the series of relative decomposition rates in (a) hydrocarbon solvent and (b) dibutyl phthalate solution:

Relative Electronegativities	Rel. Decomp. Rates Hydrocarbon Solvent	Rel. Decomp. Rates Dibutyl Phthalate
m-xylyl	m-xylyl	o-anisyl
p-anisyl	o-tolyl	m-xylyl
o-anisyl	o-anisyl	o-tolyl
1-naphthyl	p-tolyl	1-naphthyl
o-tolyl	p-anisyl	p-anisyl
p-tolyl	phenyl	p-tolyl
2-naphthyl	1-naphthyl	phenyl
phenyl	o-chlorphenyl	2-naphthyl
o-chlorphenyl	2-naphthyl	o-chlorphenyl
p-chlorphenyl	p-chlorphenyl	p-chlorphenyl
p-nitrophenyl	p-nitrophenyl	p-nitrophenyl

Close examination of the above table will reveal that excepting the three ortho-substituted radicals and 1-naphthyl, the correlation between electronegativity and decomposition rates in dibutyl phthalate is good, with the exception that the positions of phenyl and 2-naphthyl are reversed in order. In attempting to correlate decomposition rates in hydrocarbon solvent with electronegativity there is the additional reversal of the positions of p-tolyl and p-anisyl.

3. Correlation between Electronegativities and Polymerization Rates

In the following table the relative electronegativities of the eleven radicals from the diazo-thio-ethers are compared with the relative polymerization rates obtained using two different concentrations of initiator per 100 grams of monomers:

Relative Electronegativities	Rel. Polym. Rates 0.001 mol/100 gr.	Rel. Polym. Rates 0.01 mol/100 gr.
m-xylyl	m-xylyl	m-xylyl
p-anisyl	p-tolyl	p-tolyl
o-anisyl	p-anisyl	o-tolyl
1-naphthyl	o-tolyl	p-anisyl
o-tolyl	o-anisyl	o-anisyl
p-tolyl	2-naphthyl	phenyl
2-naphthyl	1-naphthyl	2-naphthyl
phenyl	phenyl	1-naphthyl
o-chlorophenyl	o-chlorophenyl	p-chlorophenyl
p-chlorophenyl	p-chlorophenyl	o-chlorophenyl
p-nitrophenyl	p-nitrophenyl	p-nitrophenyl

Again excepting the three ortho-substituted radicals and

1-naphthyl, it may be seen that the relative order of rates obtained using 0.001 moles of initiator per 100 grams of monomer is the same as the order of electronegativity, except that p-anisyl and p-tolyl are reversed. Using the larger concentration of initiator, there is the additional reversal of the positions of 2-naphthyl and phenyl. Overall correlation would seem to be somewhat better with polymerization rates than in the case of the decomposition rates. Perfect correlation could hardly be expected in view of the number of factors involved, and this will be discussed further.

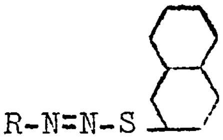
4. Correlation between Decomposition and Polymerization Rates

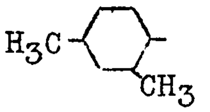
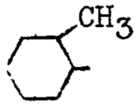
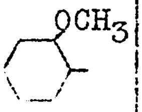
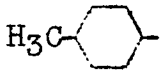
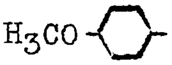
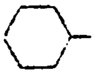
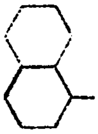
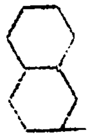
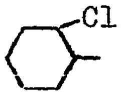
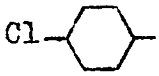
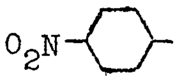
It was observed in some cases that the rate of polymerization was affected by concentration of diazo-thioether. Using very active initiators, for example 2-(2,4-dimethylbenzene-diazo-mercapto)-naphthalene (XDN), rate of polymerization increased with increasing concentration. On the other hand, however, less active initiators like 2-(benzene-diazo-mercapto)-naphthalene (PDN) (and the compounds derived from 1- and 2-naphthylamines, the chloranilines and the nitroaniline) behave in the opposite manner. Here polymerization rate was higher with lower concentration of initiator. Moderately active compounds, like 2-(p-methoxybenzene-diazo-mercapto)-naphthalene (MDN) gave polymerizations whose rates were practically independent of concentration of initiator. Data obtained on polymerization rates is summarized in Table I. To explain these results satisfactorily, it must be remembered that the diazo-thio-ethers may play a dual role in polymerizations. They not only act as initiators but may function as chain-terminators also. The diagram following Table I shows the possible functions of a diazo-thio-ether in polymerizations. If it is assumed that their chain-terminating efficiency does not depend greatly upon structure difference, while chain-initiator efficiency increases with increasing electronegativity, an explanation becomes possible. Thus, for diazo-thio-ethers producing highly electronegative radicals that are sterically unhindered, the initiating step takes precedence over the terminating step with increasing concentration. When the diazo-thio-ether produces less highly electronegative radicals, the terminating function assumes greater relative importance with increasing concentration, and consequently rates diminish. In the middle range, the importance of the two functions is apparently approximately equal, hence rate is comparatively unaffected by changes in concentration. Hence rate of polymerization may depend not only upon the rate of generation of free radicals, but also upon the rate and mechanism by which polymer chains are terminated.

In view of the influence of concentration of diazo-thio-ether on polymerization rate, it becomes difficult to decide upon a logical basis for comparison. In the following

Table I

Polymerization Rates Using Diazo Thio-Ethers



R- ↓	Rate Using 0.001 mol DTE per 100 gr. Mon.		Rate Using 0.01 mol DTE per 100 gr. Mon.		Rate 0.001 mol/rate
	% per hr.	Rel. Ph=1	% per hr.	Rel. Ph=1	0.01 mol
	13.2	2.2	16.7	3.3	0.79
	10.0	1.7	10.0	2.0	1.0
	9.9	1.6	8.5	1.7	1.1
	11.3	1.9	11.3	2.3	1.0
	10.7	1.8	9.5	1.9	1.1
	6.0	1.0	5.0	1.0	1.2
	7.9	1.3	2.8	0.56	2.8
	8.1	1.4	3.7	0.73	2.2
	3.7	0.61	0.87	0.17	4.2
	3.2	0.54	1.7	0.34	1.9
	0.25	0.04	0.19	0.04	1.3

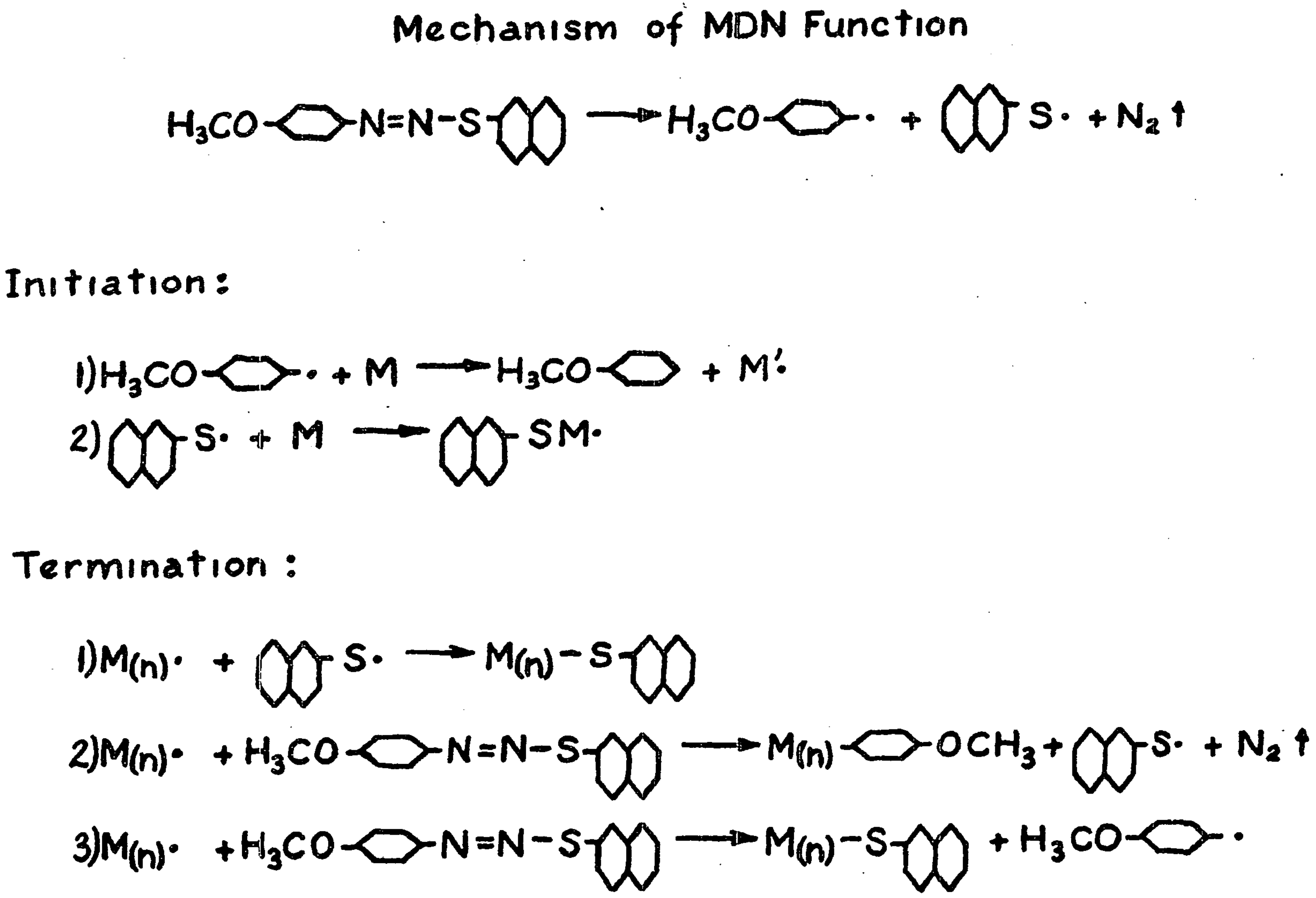

Mechanism of MDN Function
H₃CO
N=N-S
H₃CO
S· + N₂
Initiation:
1) H₃CO
+ M
H₃CO
+ M·
2) S· + M
SM·
Termination:
1) M(n)· +
S·
M(n)-S
2) M(n)· + H₃CO
N=N-S
M(n)
OCH₃ +
S· + N₂
3) M(n)· + H₃CO
N=N-S
M(n)-S
+ H₃CO

FIGURE 1

table the relative decomposition rates in the hydrocarbon solvent are compared with the polymerization rates obtained using 0.01 mole of diazo-thio-ether per 100 grams of monomers:

Diazo-thio-ethers of Type R-N=N-S-(2-naphthyl)

Radical R	Rel. Decomp. Rate in HC solvent, Ph=1	Rel. Polym.Rate Ph=1
m-xylyl	3.9	3.3
o-tolyl	3.6	2.0
o-anisyl	1.9	1.7
p-tolyl	1.2	2.3
p-anisyl	1.1	1.9
phenyl	1.0	1.0
1-naphthyl	0.9	0.6
2-naphthyl	0.4	0.7
o-chlorphenyl	0.5	0.2
p-chlorphenyl	0.3	0.3
p-nitrophenyl	0.2	0.1

Although the above correlation is reasonably close in view of the number of factors involved, it will be noticed that the ortho-substituted radicals have abnormally low polymerization rates combined with unexpectedly high solution decomposition rates. A steric factor may be indicated, since chain-initiation depends not only on the rate of generation of radicals but also upon the rate at which they can react with monomer. An ortho-substituent could well increase the instability of the diazo-thio-ether over that of the para-substituted isomer by restricting free rotation about single bonds in the molecule. The low activity of the ortho-substituted diazo-thio-ethers as polymerization catalysts may well be caused by the fact that the ortho-substituent sterically hinders, to an appreciable degree, the reactive position on the free radical. These conjectures are given support by construction of Fisher-Hirschfelder models for 2-(o-methoxybenzene-diazo-mercapto)-naphthalene and the o-methoxyphenyl radical. If the above-outlined reasoning is accepted, the apparently anomalous locations of the ortho-substituted diazo-thio-ethers in the different series, viz., solution instability and initiator-activity as compared with electronegativity, is explainable. Thus they may be expected to decompose faster than para-substituted isomers, and at the same time be less effective as initiators.

5. Decomposition Products and Mechanism of Initiator and Modifier Action

When diazo-thio-ethers are used as polymerization initiators they decompose in a very dilute solution of the monomers. Under these conditions the radicals formed have ample opportunity to react with solvent before reacting with one another. Hence in dilute solutions a maximum yield of products from reaction between radicals and the solvent, and a minimum yield of products from reaction of the radicals with each other, would be expected. In order to make the conditions of the decomposition coincide as nearly as possible with conditions during polymerizations, the decomposition was carried out in extremely dilute solution by adding a very concentrated cool solution of the diazo-thio-ether to hot tetralin at such a rate that the decomposition proceeded more rapidly than the addition.

The products obtained in the above decomposition experiment are summarized in the diagram, Figure 2. The high yield of benzene would seem to prove the following mechanism by which diazo-thio-ethers can initiate chains:

$$R\cdot + M = RH + M'\cdot \quad (M'\cdot \text{ equals } M \text{ less } H\cdot)$$

It must be kept in mind, of course, that tetralin may donate hydrogen atoms more readily than do either butadiene or styrene. Also, the temperature of decomposition was considerably higher than the usual polymerization temperature. However, the reaction mentioned must take place to a considerable extent even though these factors are considered.

Since no appreciable amount of thio-2-naphthol was formed in the decomposition, the following reaction as a mechanism for chain-initiation would seem to be eliminated:

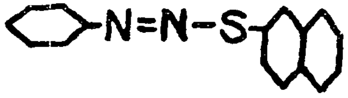
$$R'{-}S\cdot + M = R'SH + M'\cdot$$

Since no mercaptan is formed under the favorable conditions of the experiment, it hardly seems likely that it would be formed under polymerization conditions, using diazo-thio-ethers as initiators.

The presence of water during the decomposition, as for example in an emulsion system, should not substantially change

FIGURE 2

PDN Decomposition Products



264 grams - 1 mol
M.P. 70.5-72°C.
Bright yellow plates

FIGURE 2

Phenyl Part		Thionaphthol Part	
Benzene		β-β'-Dinaphthyl Disulfide	
15 plate column		Insol. in pet. ether(116g.)	
42.5 ml. B.R. 80.0-80.6°		M.P. 137-139°; lit. 139°	
Dinitro derivative :		Disulfoxide derivative:	
M.P. 89.5-90°; lit. 89.6°	0.48	M.P. 105-6°; lit. 104-6°	0.73
Phenyl Naphthyl Sulfide		Phenyl Naphthyl Sulfide	0.21
15 in. gl. hel. column		Thio Beta Naphthol	
B.R.=158-175°/1mm(50g)		Trace < 0.01g.	
M.P.=52.2°; lit. 51.8°			
Sulfone derivative :			
M.P. 116-7°; lit. 115-6°	0.21		
	0.69		0.94

Unident.-High boiling oils-Possibly tetralin dimers and/or polyphenyls the conclusions drawn above. Hantzsch and Freese[12] felt that water caused hydrolytic cleavage of the diazo-thio-ether to form mercaptan and diazonium compound. However this view was induced by the fact that disulfide was found to be present. It was assumed that disulfide was formed by air-oxidation of mercaptan formed by cleavage. In no case, however, have we been able to find evidence for hydrolysis of diazo-thio-ethers by pure water or by soap solutions, all tests for diazonium compound in such cases proving negative. Strong acid or very strong alkali is required to bring about hydrolysis forming diazonium compound and mercaptan.

It has been suggested that the diazo-thio-ethers may enter directly into chain-transfer reactions through reaction of the growing polymer chain with the diazo-thio-ether molecule, to produce either an aromatic radical or a mercaptan radical. This is shown diagramatically in Figure 1, termination reactions (2) and (3). This premise has been advanced to explain the modifier activity possessed by the compounds. In addition to this probability it should be pointed out that mercaptan radicals, generated by decomposition of the diazo-thio-ether, may themselves enter into direct combination with the growing chains, thus terminating them. This is shown in termination reaction (1), Figure 1. Since a high yield of disulfide was observed from the

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[12] loc. cit.

decomposition experiment, it seems reasonable that if a mercaptan radical is unreactive enough so that it can dimerize in high yield, then it can attain a high enough concentration to exert a considerable influence as a chain-terminator. This possibility has not been given much emphasis heretofore, since it was felt that mercaptan radicals would be too active to attain a sufficiently high concentration for functioning as chain terminators. Herein may lie explanation of many of the anomalies in rates and modifier activities encountered when only the simple hypothesis of the mercaptan radical as a chain-transfer agent is used.

EXPERIMENTAL PART

A. Preparation and Physical Properties of the Diazo-thio-ethers

Eleven different oil-soluble diazo-thio-ethers were prepared by coupling aniline, substituted anilines and the naphthylamines with thio-2-naphthol. The preparations were all similar to the process for making 2-(p-methoxy-benzene-diazo-mercapto)-naphthalene given in detail.

1. Diazotization of Base:

Materials:			
	p-anisidine	123 grams	1 mole
	water	2 liters	
	ice	1 kilo.	
	HCl (100 percent)	91 grams	(as 37 percent solution)
	$NaNO_2$	70 grams	1 mole

Finely-ground p-anisidine was dissolved in the water and acid, using mechanical stirring. Ice was added to a temperature of 0-5°C. Nitrite, dissolved in 400 ml. water, was dropped in at a rate sufficiently fast to maintain a slight excess of HNO_2, as indicated by starch-iodide test-paper. After all of the nitrite was added, the diazo-solution was allowed to stir for 30 minutes, maintaining a positive test for excess nitrite and mineral acidity as shown by Congo Red test-paper. The solution was decolorized by use of five grams each of decolorizing charcoal and filter-aid. The cold solution was then filtered through a chilled Buechner funnel into a chilled suction flask, and the filter washed with about 100 cc. of ice-water.

2. Preparation of Thio-2-naphthol Coupling Solution:

Materials:	Thio-2-naphthol	169 grams	1.05 moles
	Water	3.5 liters	
	Ice	1 kilo.	
	NaOH (10N. sol'n)	110 ml.	1.1 moles
	NaOH (" ")	190 ml.	1.9 moles

Thio-2-naphthol in finely-divided form was stirred with the water, using vigorous mechanical agitation. Ice was added to a temperature of about 10°C. The smaller portion of caustic was added all at once and the solution allowed to stir four minutes. Then five grams each of charcoal and filter-aid were added. After stirring one minute with the charcoal, the solution was filtered as rapidly as possible through a Buechner funnel onto ice. Filtration was accelerated by the use of two filter papers. A combination of a soft paper underneath, next to the perforated plate, and a hard paper on top proved effective. It was important to work rapidly and keep the solution cold during this operation, as alkaline solutions of thio-2-naphthol oxidize rapidly, with formation of insoluble disulfide, on exposure to air.

3. Coupling:

Immediately after filtration of the alkaline mercaptan solution it was placed, together with crushed ice, in a chilled, vigorously agitated container of suitable size. The balance of the sodium hydroxide was added and then the diazo solution poured into the strongly alkaline solution as rapidly as possible. The diazo solution should possess only a slight excess of nitrous acid. Any large excess was reduced by the use of sulfamic acid. Immediately after addition of the diazo-solution the mixture was tested for excess diazo by spotting on filter paper with alkaline beta-naphthol solution. If there was excess diazo, additional thio-2-naphthol was added <u>immediately</u> to remove the excess, otherwise extensive decomposition occurred.

If there was a slight excess of thio-2-naphthol in the mixture, the diazo-thio-ether separated immediately as a brownish yellow gum which solidified to a light, bright yellow solid after stirring ten to twenty minutes. As soon as solidification was complete, the solid was filtered off and washed thoroughly with cold water, then crushed and rewashed. Upon drying in a vacuum desiccator over $CaCl_2$ at room temperature overnight, the yield of the crude was found to be quantitative.

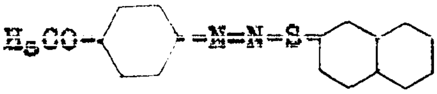
The dry crude, in batches of approximately 75 grams each, was recrystallized twice by powdering, dissolving in 700 ml. of technical diethyl ether at room temperature, decolorizing and filtering as soon as possible, and chilling immediately afterwards to -70°C. in an acetone-dry ice bath. It was found desirable to start crystallization immediately on chilling, by scratching the walls of the flask with a stirring rod. After crystallization was complete (in about 30 minutes), the product was filtered on a Buechner funnel and washed with about 75 ml. of very cold light petroleum ether. Immediately after filtering, the product was placed in a vacuum desiccator over $CaCl_2$ and subjected to high vacuum for two to three hours, in order to remove traces of ether and moisture of condensation acquired in filtration of the very cold product. Dry nitrogen was bled into the desiccator before opening. Recovery of recrystallized product was about 80 percent for the first recrystallization and slightly higher for the second. The diazo-thio-ethers had to be protected from light and stored in a cool, dry place, preferably in a desiccator in a refrigerator.

Very soluble diazo-thio-ethers, e. g., 2-(2,4-dimethylbenzene-diazo-mercapto)-naphthalene, were recrystallized from light petroleum ether instead of diethyl ether. The compound derived from p-nitraniline was best recrystallized from benzene, allowing the temperature to reach 65°C.

or slightly higher. The benzene was displaced by washing the solid product with technical diethyl ether.

The diazo-thio-ethers with their structures and melting-points are listed below:

1.) 2-(4-methoxybenzene-diazo-mercapto)-naphthalene (MDN)

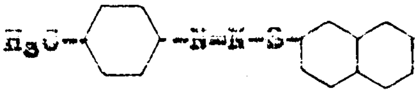


M.P. 74°C. (Literature: not reported)

2.) 2-(2-methoxybenzene-diazo-mercapto)-naphthalene

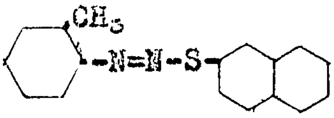
M.P. 56.5-57.5°C.
(Literature: not reported)

3.) 2-(4-methylbenzene-diazo-mercapto)-naphthalene (TDN)



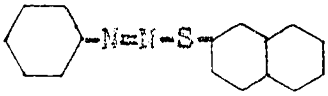
M.P. 97.5-98°C.
(Literature: not reported)

4.) 2-(2-methylbenzene-diazo-mercapto)-naphthalene



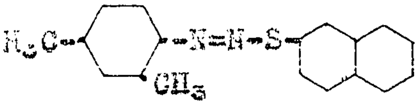
M.P. 43-44°C.
(Literature: not reported)

5.) 2-(benzene-diazo-mercapto)-naphthalene (PDN)



M.P. 70.5-72°C.
(Literature: 59.5-60.5°C.
Reference 23)

6.) 2-(2,4-dimethylbenzene-diazo-mercapto)-naphthalene (XDN)

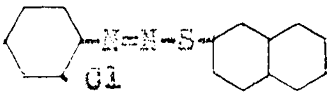


M.P. 43-44.5°C.
(Literature: not reported)

7.) 2-(4-chlorobenzene-diazo-mercapto)-naphthalene

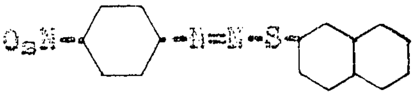
M.P. 109.5-110.5°C.
(Literature: not reported)

8.) 2-(2-chlorobenzene-diazo-mercapto)-naphthalene



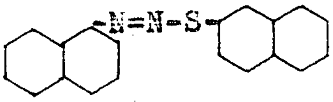
M.P. 62-62.5°C.
(Literature: not reported)

9.) 2-(4-nitrobenzene-diazo-mercapto)-naphthalene



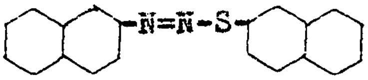
M.P. 129-129.5°C.
(Literature: not reported)

10.) 2-(1-naphthalene-diazo-mercapto)-naphthalene



M.P. 84.5-85°C.
(Literature: not reported)

11.) 2-(2-naphthalene-diazo-mercapto)-naphthalene



M.P. 107-108°C.
(Literature: 101-102°C.
Reference 23)

Melting-points of the two diazo-thio-ethers above, which had been prepared previously by Dunn and Fletcher[23], were considerably higher than the literature values. This is attributable to the fact that the Dunn and Fletcher products were not recrystallized.

B. Manometric Method for Measurement of Solution-Decomposition Rates

The decomposition rate of each of the diazo-thio-ethers was measured in dibutyl phthalate solution. It was intended that each should also be measured in mineral oil solution. However, several of the diazo-thio-ethers were insufficiently soluble in mineral oil for measurement, and it was necessary to use a tetralin-mineral oil mixture in these cases. The rate for 2-(benzene-diazo-mercapto)-naphthalene (PDN) was found to be very nearly identical in mineral oil and in tetralin (3 percent difference). In all probability, the rates in mineral oil, tetralin, and mixtures thereof can be considered together as typical of rates in a hydrocarbon solvent. The exact composition of the hydrocarbon solvent used is given in the foot-notes to Table 2, following,

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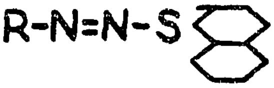
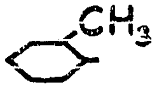
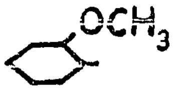
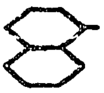
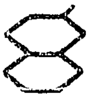
23. loc. cit.

Solution Decomposition of Diazo Thio-Ethers at 65°C.



C_0=0.04 molar

R-	Rel.Decomp. Rate $K=\frac{2.303}{t-t_0}\log\frac{C_0}{C}$		Relative Rate  = 1		K(DBP)/K(Min.Oil)
	Min.Oil K×10²	DBP K×10²	Min.Oil K×10²	DBP K×10²	
	3.39 [c]	5.06	3.97	3.18	1.3
	3.52 [c]	4.55	3.59	2.86	1.3
	1.84 [b]	5.91	1.88	3.72	3.2
	1.15 [c]	1.97	1.18	1.24	1.7
	1.05 [c]	2.0	1.07	1.26	1.9
	0.98 [c] 1.01 [d]	1.59	1.0	1.0	1.6
	0.87 [b]	2.61	0.90	1.63	3.0
	0.36 [b]	1.12	0.37	0.70	3.1
	0.46 [b]	0.97	0.47	0.61	2.1
	0.24 [b]	0.74	0.25	0.47	3.1
	0.28 [a]	0.18	—	0.11	-

[a] Solvent; 30/70, by vol., mix. of min. oil-tetralin

[b] Solvent; 50/50, by vol., mix. of min. oil-tetralin

[c] Solvent; pure min. oil

[d] Solvent; pure tetralin

Table II

which gives decomposition rates for the eleven diazo-thio-ethers in two different solvents.

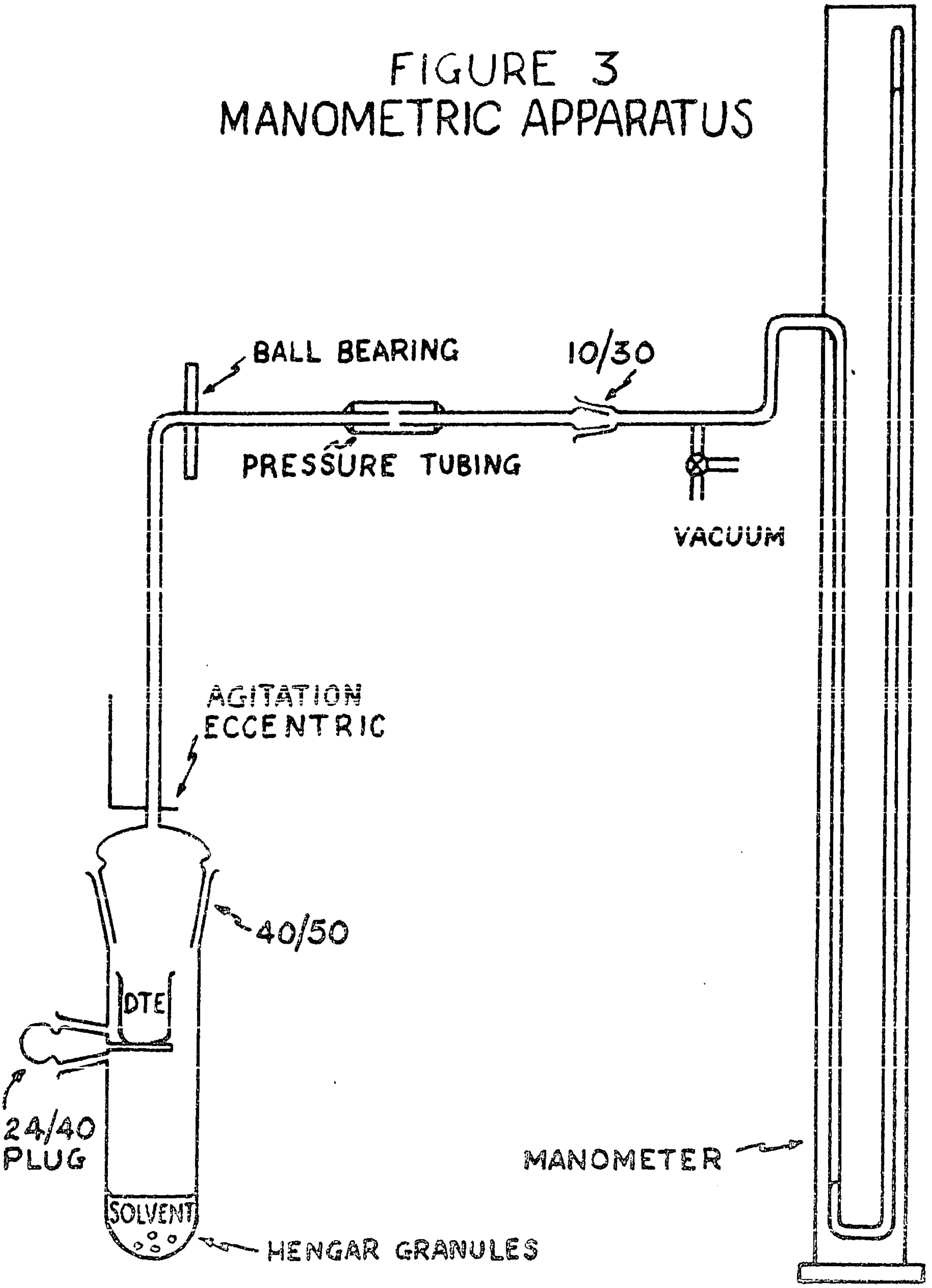
Decomposition rates of the diazo-thio-ethers in solution were measured by following the rate of nitrogen-evolution manometrically. The apparatus used is shown in Figure 3.

One one-thousandth of a mole of diazo-thio-ether was weighed into the 5-ml. glass cup, which was placed on the glass platform sealed to the end of a 24/40 ground-glass stopper as shown. Twenty-five ml. of the solvent was placed in the bottom of the reaction vessel and the entire assembly placed in a constant-temperature bath up to the capillary tubing above the reaction vessel. Heavy-walled capillary tubing connected the reaction vessel through a ball-bearing and pressure-tubing connection to a 10/30 joint on the manometer. The volume of the reaction vessel was 166 ml., while the non-thermostatted portion of the capillary tubing, including the manometer to the zero-line, had a volume of 3.5 ml. The manometer itself was made from capillary tubing, and the change in volume of the system throughout an experiment was negligible. Calculations of error, due both to volume change and to the difference in temperature of the non-thermostatted portion of the system, were made and found to be within the experimental error of the measurements.

The solvents used were dibutyl phthalate, mineral oil, and tetralin. With either of the first two, the system was

FIGURE 3

MANOMETRIC APPARATUS



evacuated and allowed to come to equilibrium at about five millimeters pressure. When tetralin was used as a solvent, the starting pressure was about 100 millimeters. Checks at different starting pressures, using mineral oil as solvent, revealed no noticeable differences in rate. Temperature used for the comparisons was 65.3°C.

When the system was at temperature and pressure equilibrium, the cup of diazo-thio-ether was dumped into the solvent, zero time and the pressure reading being recorded at the instant of dumping, using a stop-watch. When quite unstable compounds like that derived from m-xylidine were used, it was found that an appreciable amount of the diazo-thio-ether decomposed in the solid state in the cup before dumping. This difficulty was eliminated by placing 3 ml. of cold solvent, withheld from the amount in the bottom of the reaction vessel, in the cup with the diazo-thio-ether. By working rapidly the assembly could be arranged and the reaction started before a noticeable amount of decomposition occurred. Although the system, in such cases, was not at exact temperature equilibrium at the beginning of the reaction, no irregularities were found to occur in the range of twenty to eighty percent reaction, from which the rate was calculated.

The reaction vessel was agitated vigorously at a frequency of approximately 200 cycles per minute through a 3/4-inch amplitude at the bottom of the vessel by means of a motor-eccentric arrangement. The ball-bearing bore the load caused by the weight of the reaction vessel, and the rubber hose connection absorbed the torque created by the pendulum motion.

Decomposition rates were not affected by glass surface -area. Identical rates were obtained whether the vessel contained one or one hundred Hengar granules or five grams of powdered glass. In practice the vessel always contained powdered glass to facilitate equilibration of the evolved nitrogen though no experimental evidence was obtained to show that this precaution was necessary. Also, it was found that more uniform values of final pressure-change were obtained if the solvent, containing the powdered glass, was de-gassed shortly before beginning a run. This was done by heating for several minutes almost to the boiling-point of the solvent at about 2 mm. pressure, and then allowing the system to cool below room temperature while vacuum was maintained.

The decompositions were not autocatalytic. In one experiment, involving decomposition of 2-(2,4-dimethylbenzene-diazo-mercapto)-naphthalene (XDN) in mineral oil, the rate-constant obtained was 0.0389/min. A second run made in exactly the same manner but using as solvent the solution of decomposition products obtained from the first run, gave a constant of 0.0395/min. Such a difference was well within the experimental error of reading the manometer.

In some instances any departure of the data from a first-order reaction was not discernible. For example, in the decomposition of 2-(p-methoxybenzene-diazo-mercapto)-naphthalene (MDN) in both mineral oil and dibutyl phthalate solution, a first-order rate constant was obtained as far as could be ascertained with the precision of the measurements. In Figure 4 is shown the data for decomposition of this compound in dibutyl phthalate. Pressure-increase, in millimeters of mercury, is plotted versus time. Then the logarithm of a function of the concentration, namely $c' = (\Delta P_f - \Delta P_t)/\Delta P_f$, is plotted versus time in minutes. If there was no noticeable regular curvature in the latter plot, and if the readings were properly spaced with respect to time, the "most probable value" of the rate-constant was selected by the method of Roseveare[39]. If, as in most cases-, especially where dibutyl phthalate was used as solvent-, there was a slight, regular curvature to the plot of log c' versus time, an approximation was made for purposes of comparison by plotting the best straight line through the data in the range 20-80 percent by the method of least-squares. Since only a comparison was sought and a considerable number of runs were to be made, the data was not weighted by the laborious method suggested by Reed and Theriault[40], and zero error in measurement of time was assumed in the use of the least-squares method of computation. From the slope of the least-squares straight line, the rate-constant followed.

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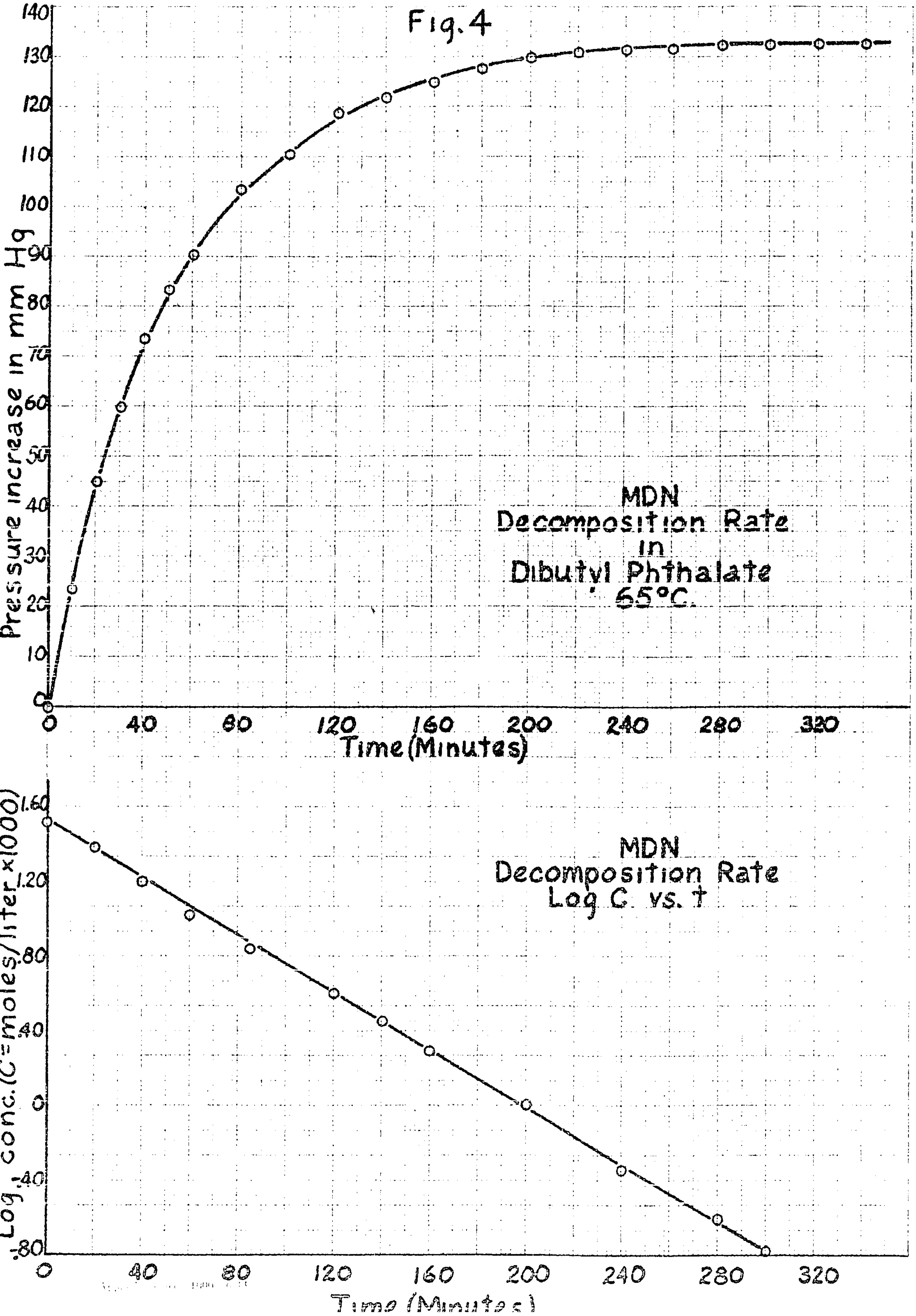
[39] Roseveare: J. Am. Chem. Soc. 53, 1651 (1931)

[40] Reed and Theriault: J. Phys. Chem. 35, 673 (1931); ibid. 35, 950 (1931)

Fig. 4


MDN
Decomposition Rate
in
Dibutyl Phthalate
65°C.
Pressure increase in mm Hg
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
Time (Minutes)
0
40
80
120
160
200
240
280
320
MDN
Decomposition Rate
Log C vs. t
Log. conc. (C = moles/liter × 1000)
1.60
1.20
.80
.40
0
-.40
-.80
Time (Minutes)

C. Determination of Polymerization-Initiator Activity

Most of the diazo-thio-ethers for which decomposition rates were determined had been previously evaluated as polymerization promoters, using the Fryling[24] method of following the course of the reaction taking place in sealed tubes. However, as has been mentioned before, due to insufficient agitation in tubes, rates determined in this manner are not reliable. Hence polymerization rates at 50°C. were re-determined for the eleven diazo-thio-ethers concerned, using six-ounce crown-capped bottles and following the course of the reaction by means of assay for total solids on samples of latex. The purified diazo-thio-ethers were used in two different concentrations, viz., 0.01 mole DTE per 100 grams of monomers and 0.001 mole DTE per 100 grams monomers.

The recipe adopted as standard for evaluation of the activities as polymerization initiators was as follows:

Butadiene	72 grams
Styrene	28 grams
Water	180 grams
Soap	5 grams
Diazo-thio-ether	As noted

In practice, in order to use six-ounce bottles, this recipe was multiplied by a factor of six-tenths. Self-sealing crown caps described by Harrison and Meincke[41] were used, together with the hypodermic syringe sampling device described by Houston[42]. Progress of the reaction was determined period-

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[41] Harrison and Meincke: *Self-Sealing Bottle Caps in Bottle Polymerizations*. Rubber Reserve Co. technical report from the B. F. Goodrich Co.

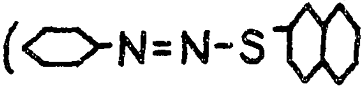
[42] Houston: *Device for Sampling Latex*. Rubber Reserve Co. Report No. CR-545, from B. F. Goodrich Co.

ically through the run, in each case, by removing samples of the latex. Percentage conversion is determined by means of determination of total solids content of the latex, obtained by evaporation to dryness of a weighed sample. Assigning a numerical value to the polymerization rates is somewhat arbitrary since, in many cases, the rate-curves were not linear. Rates were assigned that represented the best average rate in percent per hour over the earlier range of conversion, before the rate began to diminish and the curve to flatten out.

D. Study of Decomposition Products

One mole (264 grams) of 2-(benzene-diazo-mercapto)-naphthalene, designated as PDN, was decomposed in tetralin at 100°C., and the greater part of the decomposition products identified. The diazo-thio-ether was prepared from aniline and thio-2-naphthol as described in detail earlier for 2-(p-methoxybenzene-diazo-mercapto)-naphthalene (MDN). In this case, however, the coupling was carried out in a solution of sodium carbonate, even though the reaction is perfectly satisfactory if caustic is used as before. The product was recrystallized from ether twice, as described before. Pure product proved to be brilliant golden-yellow plates, melting at 70.5-72°C.

The decomposition was carried out in the all-glass apparatus shown in Figure 5. The tetralin used as solvent was fractionated through a 15-plate column just prior to use, the cut distilling at 204-205.5°C. (uncorr.) being used

Apparatus for Decomposition of
PDN( in
Tetralin

Purified PDN-one mol (264 grams) in tetralin (204-205.5°)-700 ml.-run into 100 ml. tetralin in flask. T = 100 °C.

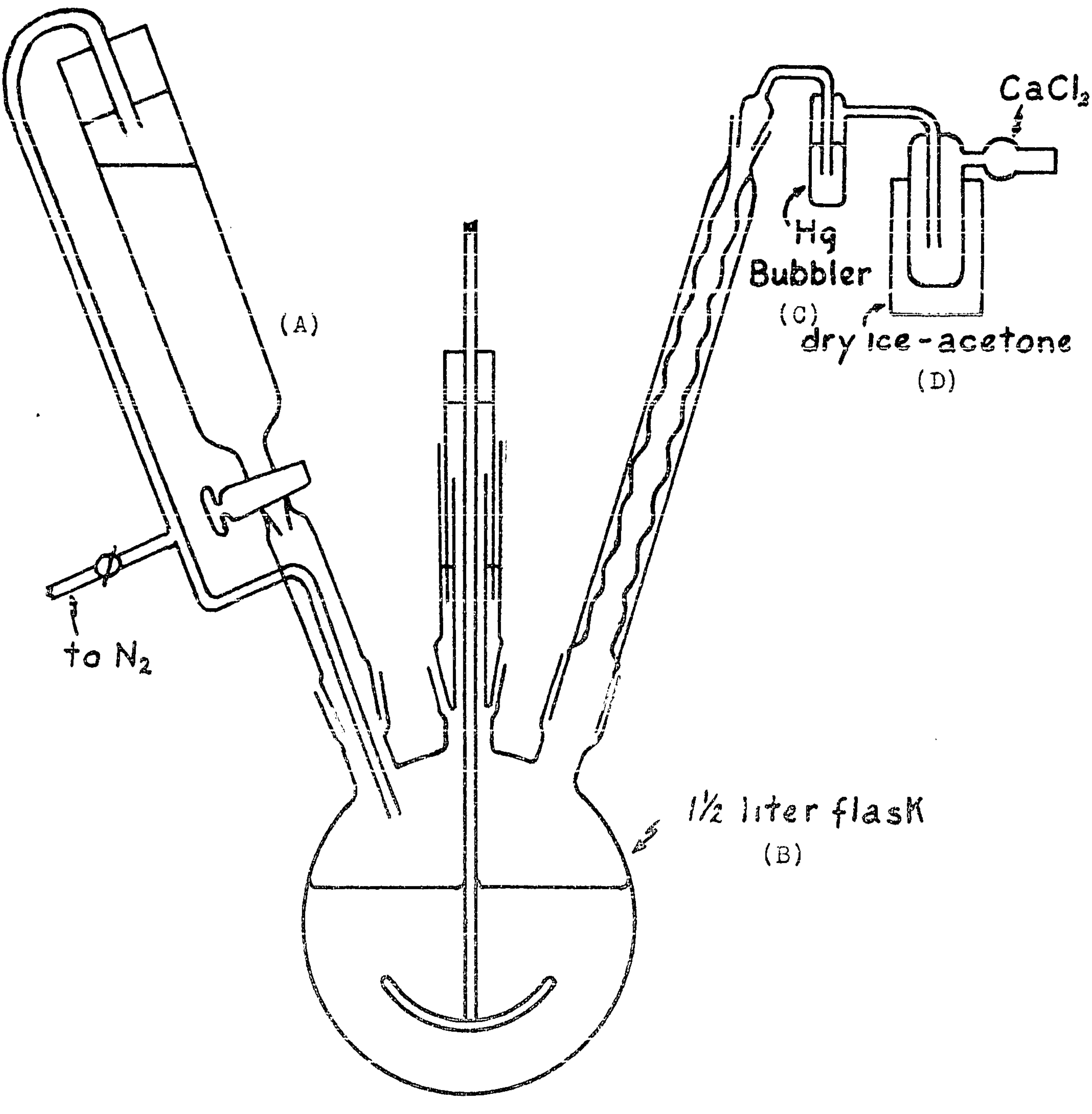


FIGURE 5

in the experiment.

The one-and-one-half liter flask in which the decomposition occurred was closed to the atmosphere by means of a mercury-seal stirrer and a mercury bubbler at the outlet side of the condenser. The entire system was flushed thoroughly with anhydrous nitrogen from a tank connected to the dropping-tube (A). On the outlet side of the mercury bubbler (C) were connected two traps in series (D), which were kept at -70°C. throughout the experiment. At the start, 100 ml. of tetralin were placed in the flask (B) which was kept in an oil-bath at 100°C. The mole of diazo-thio-ether was dissolved in 700 ml. of tetralin and this solution was slowly (three hours) dropped into the hot tetralin in the flask. Nitrogen evolved was passed out through the mercury bubbler and the two traps. After all the diazo-thio-ether solution had been added, the temperature was maintained at 100°C. for two hours, after which the reaction mixture was allowed to cool and stand overnight. Care was taken throughout to avoid the introduction of air into the system.

The two dry-ice traps were used primarily to trap entrained benzene, which was expected to be one of the principal products. A total of about 4 ml. of liquid was found in the first trap and a trace in the second. These were carefully added to the reaction mixture.

Analysis for Thio-2-naphthol: A ten-ml. aliquot of the reaction mixture was extracted with a dilute sodium hydroxide solution. Upon acidification of the aqueous layer, a very faint turbidity indicated no more than a trace of thio-2-naphthol. Titration of additional small aliquots by the Kolthoff amperometric technique[43] indicated that the entire reaction mixture contained less than 0.01 gram of the mercaptan.

Analysis for Benzene: The entire reaction mixture was next steam-distilled to separate the solvent and volatile reaction products from the sulfides. The volatile oil was dried with calcium sulfate and fractionated through a 15-plate column. Forty-two and one-half ml. of pure benzene (boiling range 80.0-80.6°C) was obtained. The dinitro-derivative melted at 89.5-90°C. (uncorr.), while meta-dinitrobenzene melts at 89.8°C. This amount of benzene represented 0.48 moles, or 48 percent of the teoretical.

Determination of 2,2'-Dinaphthyl Disulfide and Phenyl-2-naphthyl Sulfide:

The non-steam-distillable portion of the original mixture weighed 235 grams. It was a light-tan, waxy solid. It was found that dinaphthyl disulfide is quite insoluble in light petroleum ether while all the other reaction-products are quite soluble in that solvent. All of the products, including the disulfide, are quite soluble in benzene. Consequently, a simple assay for dinaphthyl disulfide was based upon these observations. Seventy-five grams of the waxy solid was dissolved in 75 ml. of boiling

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[43] Kolthoff and Harris: *Determination of Mercaptan in Latex by Amperometric Titration.* Rubber Reserve Co. technical report No. CR-62, from University of Minnesota

benzene. This hot solution was then poured very slowly into 500 ml. of vigorously agitated petroleum ether. The disulfide precipitated almost quantitatively and was filtered off, washed thoroughly with light petroleum ether, and dried overnight at 50°C. Weight was 37 grams. This corresponds to a yield of 110 grams from the entire mixture, or 73 percent of the theoretical. One recrystallization from benzene gave a melting-point of 137-139°C. The literature melting-point of dinaphthyl disulfide is 139°C. A portion of the disulfide was oxidized to the disulfoxide with hydrogen peroxide in glacial acetic acid. It melted at 105-106°C. whereas the literature value is 104-105°C.

The phenyl-2-naphthyl sulfide and any other products of the reaction remained in the benzene-petroleum ether filtrate from the above separation. The solvent was removed from this mixture and the oil remaining was subjected to prolonged steam-distillation, in order to remove all traces of tetralin remaining after the earlier steam-distillation. The residue was taken up in ether, dried, and the ether removed. The remaining oil was then distilled at a pressure of 1.5 mm. through an 8-inch column packed with glass helices. Sixteen grams of product distilled between 160° and 200°C. The literature boiling-point for the sulfide is 226°C./11 mm. The product was an oil which readily crystallized from methanol upon cooling with dry-ice. After two recrystallizations from methanol, the pure white solid melted at 52.2°C. Literature melting-point for phenyl-2-naphthyl sulfide is 51.8°C. Oxidation in glacial acetic acid with cold potassium permanganate gave the sulfone; glistening plates with a melting-point of 116-117°C. Literature value is 115-116°C. Sixteen grams of the sulfide from the 75-gram sample is equivalent to fifty grams from the entire batch, or a yield of 21 percent of the theoretical.

Other products: No additional products were identified although the above analyses leave 69 grams of product unidentified. About half of this material distills from 200-280°C. at 1.5 mm. pressure, leaving a tarry residue. The high-boiling oil was not identified, but it was suspected to contain some dinaphthyl disulfide not separated in the precipitation with petroleum ether. Tetralin dimer or polymer and possibly some meta-terphenyl may also be present.

Thio-2-naphthol from Dinaphthyl Disulfide: It was interesting to observe that when a 50-gram sample of the original waxy solid from the first steam-distillation was distilled through a 20-inch helices-packed column at 1 mm. pressure, thio-2-naphthol was collected in good yield. When the pot temperature reached somewhat above 200°C., a vigorous reaction ensued, and the odor of hydrogen sulfide was noticed. After a time the reaction moderated, and the distillation was continued. Twenty-one grams of practically pure thio-2-naphthol were collected between 110°-116°C/1 mm. The product was completely soluble in dilute, aqueous caustic, and, after precipitation with acid, the pure compound melted at 81-81.5°C. Literature value was 81°C. To complete the identification, it was converted to 2,4-dinitrophenyl-2-naphthyl sulfide, melting at 141.5-142.5°C.

SUMMARY

1. Rates of solution-decomposition at 65.3°C were determined for eleven diazo-thio-ethers of type R-N=N-S-R'; where R' was always 2-naphthyl, and R- was an aromatic radical chosen, in each case, to give a wide variance in electronegativity for the eleven compounds. Two different solvents were used; one polar, the other non-polar. Decomposition was very nearly a first-order reaction in all cases. Decomposition rates were higher in the polar solvent. Decomposition rates correlate roughly with electronegativity of the radical R, with the exception of ortho-substituted radicals which tend to cause abnormally rapid decomposition.

2. Activities of the diazo-thio-ethers as polymerization-initiators were determined, using two different concentrations of initiator in a standardized formula. An arbitrary numerical value for the polymerization rate was assigned in each case. Polymerization rate is affected by concentration of initiator when very active or very inactive diazo-thio-ethers are used. Compounds

of moderate activity are relatively independent of concentration of initiator, when used in polymerizations. Ortho-substituted radicals R give initiators of unexpectedly low activity; otherwise correlation of electronegativity and initiator-activity is fairly close.

3. Solution-instability and polymerization-initiator activity are compared for the eleven diazo-thio-ethers.
4. A diazo-thio-ether was decomposed in an anhydrous, organic solvent and the products of decomposition identified on a quantitative basis. Aromatic free radicals generated by diazo-thio-ether decomposition strip hydrogen from tetralin at 100°C.
5. It is proposed that the radical R•, formed from decomposition of the diazo-thio-ether initiator, may initiate chains, in emulsion polymerization, by stripping hydrogen from a monomer molecule as well as by combining with it to form an activated adjunct.
6. It is further proposed that the mercaptan radical, R'-S•, formed by the decomposition of the diazo-thio-ether, may attain a high enough concentration, due to its inherent inactivity, to act as a chain-terminator as well as initiator.