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THE EFFECT OF GAMMA RADIATION ON THE REACTIONS OF HYDROGEN SULFIDE WITH OLEFINS

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DEDICATION

To all my friends
who make life so
meaningful

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ABSTRACT

The addition reactions of hydrogen sulfide with propylene, butene-1, butene-2 and isobutene were studied under the influence of gamma radiation from a cobalt-60 source. The reactions were conducted in the liquid phase, without the use of solvent, in batch reactors made by Pyrex glass. The products of the reactions were identified by standard analytical techniques, and the product distribution was quantitatively analyzed by gas-liquid chromatography.

The addition reactions of butene-1, butene-2 and isobutene with hydrogen sulfide were studied at a temperture of -78°C, radiation intensities of 1330-1570 rads/min and with an equimolar reactant concentration in the reaction mixture. For the propylene-hydrogen sulfide reaction, the investigation was extended to study the reaction kinetics. The variables studied in this case were, (a) radiation intensity between 30.6 and 1570 rads/min, (b) mole fraction of the reactants between 0.2 and 0.8, and (c) temperature range of -78°C to -25°C.

The G-values obtained for all the addition reactions studied were greater than 10^3, suggesting a chain mechanism. The identification of the products of the reaction indicated that the mode of addition is "abnormal", i.e., contrary to Markownikoff's rule. A free radical mechanism initiated by radiation through generation of HS· radicals is postulated. The free radical mechanism is supported by the observation that oxygen has an inhibiting influence on the reactions. The reactivities of the olefins followed the order - propylene > butene-2 > isobutene > butene-1.

For the propylene-hydrogen sulfide addition reaction the major products were found to be n-propyl mercaptan and n-propyl sulfide. The experimental rate data obtained for the reaction conducted at $-78^{\circ}C$ with equimolar reactant concentration and at low intensities of radiation (30-150 rads/min) were correlated by the expression

$$R = -\frac{d[H_2S]}{dt} = 8.5 \times 10^{-5} I^{0.5} [C_3H_6][H_2S] \text{mole/(liter)(min)}$$

At higher intensities, however, the reaction rate seemed to become independent of the radiation intensity. The variation of composition between fourfold excess of the hydrocarbon (propylene) and fourfold excess of the addend (hydrogen sulfide) indicated an influence of both the reactants on the initial reaction rate. The analysis of the temperature effect between $-78^{\circ}C$ and $-25^{\circ}C$ showed only minor effects. The overall activation energy for the addition reaction was estimated as approximately -650 cal/mole.

Several kinetic expressions are derived on the basis of the free radical mechanism proposed. These expressions are compared with the above-mentioned kinetic correlations and both the mechanism and the derived expressions are utilized to analyze the effects of the reaction variables.

I. INTRODUCTION

The ionizing properties of high energy nuclear radiations suggest their application in the initiation of chemical reactions. Interest in this field, known as radiation chemistry, has grown at a rapidly increasing rate since the advent of the nuclear reactor and subsequent availability of artifical radioisotopes. A number of books have appeared recently covering both the theoretical aspects of the effects of radiation on chemical compounds and their reactions, and industrial utilization of radiation energy.(16,18,20,45,89)

The highly energetic radiations include electromagnetic radiations such as X-rays and gamma rays, and corpuscular radiations such as protons, neutrons and alpha and beta particles. The term "ionizing radiation" usually covers all these types of radiations, even though the electromagnetic radiation and neutrons cause ionization only indirectly. The fact that it should cause ionization puts the lower limit on the energy of radiation at about 10 ev (equivalent to electromagnetic radiation of 100 A°U. wavelength) since this represents the binding energy of an outer electron to the nucleus.

Besides the production of ions, high energy radiations also produce other transient and reactive species such as excited molecules and free radicals, which are also known to occur in photochemical reactions initiated by less energetic radiations such as ultra-violet and visible light. Hence, the overall, chemical effects in radiation chemistry are quite often similar to those in photochemistry. It may also be noted here, that certain chain reactions which are initiated by transient species such as free radicals and ions, by using conventional methods, are also found to occur under the action of ionizing radiation. Such chain reactions are of great interest in radiation chemistry from the viewpoint of commercial application, since large yields of products and high efficiency in utilization of radiation energy are obtained.

Several addition reactions of olefins occur by chain mechanisms. One class of such reactions is the additions of compounds containing sulfhydryl group (SH group) such as hydrogen sulfide or organic mercaptans, to olefins. Thus, it has been shown that the reaction between propylene and hydrogen sulfide may be initiated by free radicals produced from photodissociation of hydrogen sulfide effected by light of wavelength below 2800 A°U.(92)

The purpose of this study was to investigate the effect of cobalt-60 gamma radiation on the addition reactions of the olefins, propylene, butene-1, butene-2 and isobutene, with hydrogen sulfide. Even though the products formed in these reactions do not presently have commercial importance, the reactions were selected as a guide to further studies in similar organic synthesis. Another objective of this study was to develop possible mechanisms of the addition reactions by investigation of the products formed and the kinetics of the reactions. The propylene-hydrogen sulfide reaction was chosen to study the detailed effects of various parameters such as the intensity of the radiation, temperature of the reaction, and the composition of the reaction mixture. It was hoped that this study would provide some information regarding basic processes in radiation chemistry.

II. THEORY AND BACKGROUND OF RADIATION CHEMISTRY

A. Interaction of Radiation With Matter

When ionizing radiation passes through matter its energy is transferred to the absorbing medium by various physical mechanisms. Its duration is of the order of 10^{-13} seconds or less. (25) This primary act of energy dissipation is followed by the formation of transient species which then react to form the final chemical products. Various aspects of the physical mechanisms and the transient species are discussed below with particular reference to gamma radiation.

1. Physical Mechanisms

The major processes for interaction of high energy gamma radiation with matter are (a) photoelectric absorption in which a photon transfers its entire energy to an electron; (b) Compton effect in which only a fraction of the photon energy is transferred to an electron and a modified photon with lower energy emerges; (c) pair production for photons with energies above 1.02 Mev. in which a photon disappears with the formation of a positron and an electron.

The relative contributions of these three effects depend upon the absorption medium and the energy of the incident photon, and have been carefully examined for certain mediums. (2) The Compton effect predominates almost exclusively in the range of photon energies used in most chemical studies, namely 200 kev to 2 Mev. The energy distribution of Compton electrons depends on the energy of the incident photon. For 1 Mev gamma photons the average energy of the recoil electrons is 440 kev. (59)

The absorption of energy by the Compton effect is proportional to the number of electrons per gram of material. For the present study with cobalt-60 gamma radiation of energy 1.17 and 1.33 Mev, this effect is considered to be the only absorption mechanism.

2. Chemical Phenomena

Subsequent to the absorption of radiation, the two fundamental actions of radiation are formation of ions and excited molecules. In the case of Compton scattering such ionization and excitation can be caused by the electrons, while the scattered photons of reduced energy interact further as already discussed. These transient species can then undergo secondary reactions, such as electron capture, charge neutralization and molecular dissociation.

(a) Ionization and Neutralization

Ionization is a process in which an orbital electron is removed from its parent nucleus, giving rise to a free electron and a positively charged nucleus:

$$AB \rightsquigarrow AB^+ + e$$

Such a process could occur in various interactions, for example, that of an electron and a molecule of the absorbing medium. Such ions are often unstable and may dissociate:

$$AB^+ \longrightarrow A^+ + B$$

This process could also occur in one state, such as:

$$AB \rightsquigarrow A^+ + B + e$$

The ionization potentials of various gases have been reported in literature.(20) Owing to the other causes of energy loss, the energy absorbed per ion-pair produced in many gases is higher than the ionization potential. The excess energy is usually thought to be associated either with the ion or the molecule or both. In organic molecules the bond energies are lower than ionization energies. Thus the ionization potential for H_2, H_2S and C_3H_6 are 15.4, 10.42 and 9.7 ev respectively.

The average energy dissipated per ion-pair can be determined in gases, where the number of ionizations can be measured directly. In condensed systems, however, this is not possible and is commonly assumed to be the same as in gases.

All electrons that are ejected from the molecules of the absorbing medium lose their kinetic energy by ionizing or exciting other molecules until they are thermalized. The fate of the thermalized electron in condensed media is still under dispute.(75)

The electron can lose its freedom in a variety of processes as follows:

(1) The electron could recombine with a positive ion, forming an excited molecule (indicated here by star as superscript).

$$AB^+ + e \longrightarrow AB^*$$

This step will be discussed further in the next section.

(2) The electron could be trapped by a neutral molecule, forming a negative ion:

$$AB + e \longrightarrow AB^-$$

This reaction is of great importance, since some compounds like oxygen can act as an efficient electron trap. Thus

$$O_2 + e \longrightarrow O_2^-$$

occurs readily. Hence the presence of an impurity having a high electron affinity significantly reduces the radiation-chemical yield.

(3) The electron could be captured and cause dissociation if the molecules of the irradiated medium contain atoms or groups of atoms having electron affinities greater than their binding energy to the rest of the molecule:

$$AB + e \longrightarrow A + B^-$$

A is usually a free radical and B^- a free radical ion.

The positive and negative ions formed in various processes may interact with each other to form excited molecules. This happens mostly in systems with efficient electron traps, when large concentrations of negative ions are likely.

Excitation

The radiation-induced excitation closely resembles the corresponding process in photochemistry. Thus:

$$A\ B \rightsquigarrow A\ B^{*}$$

$$A\ B + h\nu \longrightarrow A\ B^{*}$$

However, in radiation-chemical reactions a large variety of excited states are produced and hence the products formed may be different. The excited state produced in this manner, however, has a lower energy than the one produced by an ion-electron recombination.

The excited molecules can react in the following way:

(1) Dissociation into free radicals:

$$A\ B^{*} \longrightarrow A^{\cdot} + B^{\cdot}$$

Here the dot represents a free electron (also known as an unpaired or odd electron). This reaction is considered to be very important in many radiation-chemical processes. An important effect, known as the Franck-Rabinowitch "Cage" effect, suggests that unless the decomposition is an energetic one there is a possibility that radicals may recombine within the solvent cage, particularly in condensed phases, leading to no net reaction.

(2) The excited molecules can undergo dissociation by themselves or react with other molecules as follows:

$$A\ B^{*} \longrightarrow C + D$$

$$A\ B^{*} + C\ D \longrightarrow \text{Products}$$

Free Radicals

In many radiation-chemical processes, free radicals are mainly responsible for chemical change. This conclusion is based on various observations. Several free-radical chain reactions are initiated by ionizing radiation in a manner similar to the initiation by ultra-violet light or by chemical initiators such as some organic peroxides. In all these cases some inhibitors are equally effective in retarding a chain reaction.

A typical free radical possesses a single unpaired electron. Considering the following processes

$$A: + B\,C \longrightarrow A\,B + C:$$

$$A\cdot + B\,C \longrightarrow A\,B + C\cdot$$

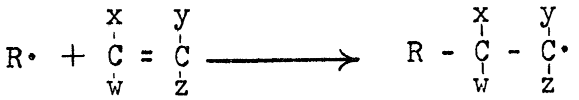
the former represents a heterolytic reaction, while the latter is a typical radical reaction. In the case of ionization, $RX \rightsquigarrow RX^{+\cdot} + e$, the parent molecule-ion can be regarded as a positively charged free radical (indicated by $+\cdot$).

Walling (95) and Steacie(87) have discussed the important free radical reactions. The following is a brief summary of these reactions.

(1) Exchange reactions:

$$R_1\cdot + XR_2 \longrightarrow R_1X + R_2\cdot$$

(2) Addition reactions to unsaturated molecules:



$$R\cdot + \underset{w}{\overset{x}{C}} = \underset{z}{\overset{y}{C}} \longrightarrow R - \underset{w}{\overset{x}{C}} - \underset{z}{\overset{y}{C}}\cdot$$

(3) Destruction reactions:

(a) Combination: $R_1\cdot + R_2\cdot \longrightarrow R_1R_2$

(b) Disproportionation: $R_1\cdot + R_2CH_2CH_2\cdot \longrightarrow R_1H + R_2CH{=}CH_2$

For normal hydrocarbon radicals, the activation energy for exchange reactions involving H atoms is of the order of 8 - 12 kcal/mole. The addition reactions in general require a slightly lower activation energy than the exchange reactions. Combination requires no activation energy, while disproportionation requires very little energy.

The most direct way of studying free radicals is by electron spin resonance, sometimes called paramagnetic resonance.(45) The existence of free radical intermediates in radiated systems has been demonstrated by the use of reactive solutes as scavengers, such as quinones,(24) diphenylpicrylhydrazil(24) and iodine.(82)

Energy Transfer

In many binary mixtures it is observed that charge transfer or excitation transfer could occur between two unlike molecules, such as:

$$A^+ + B \longrightarrow A + B^+$$

$$A^* + B \longrightarrow A + B^*$$

For charge transfer processes to occur, the ionization potential of A must be higher than that of B. Such reactions can be used to increase ionic yields in certain systems by the addition of inert gases, such as argon, helium, etc. Transfer of excitation, however, is a more complex phenomenon.

A particular case of excitation transfer occurs in some cases involving aromatic compounds and is commonly known as "protection action." In this case the excitation energy is transferred from the excitation region to some molecule or group which possesses a mechanism for dissipation of this energy. Such a phenomenon is described for aromatic sulfides by Krongauz.(57)

The energy transfer processes mentioned above could be utilized to distinguish between "direct action," whereby molecules interact with radiation and produce chemical change, as opposed to "indirect action," whereby the primary interaction of radiation takes place with some inert molecules.

The "indirect effect" most often mentioned in the case of radiation effects on aqueous solutions usually refers to the reactions of $H\cdot$ and $OH\cdot$ radicals produced in the radiolysis of water with various solutes.

3. Distribution of the Transient Species

The elementary processes producing transient species have been described in the previous section. The nature and distribution of the transient species produced depend upon the type of radiation and the nature of the medium being radiated. This distribution together with the various terms that are used to describe it, is discussed below.

The so-called "spurs," or "clusters," are sites of dense ionizations and excitations and are produced both by the primary effect of the incident radiation and by the secondary particles, such as δ-electrons, along the path (or'track') of the ionizing particle. Once a cluster is formed, the concentration of active species decreases rapidly, owing to diffusion and chemical reaction. The problem of ion difussion and recombination in spurs has received widespread attention and has been treated theoretically.(34, 56)

The most useful quantitative description of this distribution is given in terms of average energy loss per unit path (linear energy transfer or LET) or in terms of the ion density, i.e. the average number of ion pairs produced per unit length of path. For cobalt-60 gamma radiation the ion density is about 10 per micron and the corresponding LET is about 0.3 kev/micron. This value of LET represents a mean,(89) and it should be noted that the LET at the end of a track or for a δ-ray is much higher. As opposed to the small value of LET for cobalt-60 gamma radiation, the value of LET for Polonium α-particles is as high as 150 kev/micron.

The influence of LET is significant in radiation chemistry of water.(2) With high LET radiation, the probability for the recombination reaction of the primary radicals H· and OH· produced in dense tracks is high. The result is the formation of molecular products and a reduction in the number of radicals which could diffuse into the body of the solvent for homogeneous reaction with any available solute. Thus the number of ferrous ions oxidized by gamma radiation in aqueous solution of ferrous solfate is 15.5 per 100 ev of evergy absorbed; whereas only a third as many ferrous ions are oxidized by α-rays from Polonium. The influence of LET on radiation chemistry of organic compounds, except in the case of some aromatic substances, however, is not considered to be important.(99)

B. Reaction Mechanisms and Overall Chemical Effects

The historical development of radiation chemistry has been marked by shifts in interpretations regarding the mechanisms of the reactions of the transient species which produce the final chemical change.(99) Lind(61) studied the effect of α-particles from radon, on gas-phase reaction of acetylene yielding cuprene as a product. He postulated the ion-cluster theory which suggested that a number of molecules of acetylene reacted by forming clusters around the ions formed by the effect of radiation. This theory was disputed, however, by Eyring, Hirschfelder and Taylor(28) who placed major emphasis on processes parallel to those of photochemistry, e.g. excitation with ensuing decomposition of excited molecules to yield free radicals. Recently, however, ion-molecule reactions have regained a considerable amount of attention, particularly in gas-phase reactions at low pressures.(88,90)

At present it is believed that the chemical effects of radiation in the gas phase may be caused by both the kinds of reactive species, namely ions and free radicals. In the condensed phase, however, it is generally believed that electron capture after an ionization event is almost instantaneous. A justification for this is that it is shown by approximate calculations that electrons rapidly lose their excess energy in liquids within the range of the strong coulombic force between the parent ion and the electron.(30) The main reactive species in that case are the free radicals.

C. Radiation Yield - G-Value

Radiation yeilds are usually given in terms of the G-value introduced by Burton.(13) The G-value is defined as the number of molecules reacted per 100 electron-volts of absorbed energy. The ionic yield M/N, which was used in early studies, is defined as the number of molecules reacted per ion-paired formed. The two values are related by W, the mean energy required to form one ion-pair.

III. LITERATURE REVIEW

A. Conventional and Photolytic Methods in Addition Reactions

The addition reactions of hydrogen sulfide with simple olefinic compounds have been studied at high temperatures, generally above 200°C, and with various catalysts. Mayo(63) has presented a summary of such investigations. Duffey (26) studied the reaction of hydrogen sulfide and propylene between 200°C and 300°C and with a number of catalysts, including activated fuller's earth, activated charcoal, silical gel, and aluminum oxide. He obtained a maximum conversion of 17% at 200°C and noted that the mercaptan formed decreased with increasing temperature. It was reported that the yield of alkyl sulfide was very little. Barr(9) reported slightly higher yields for the same reaction with a nickel sulfide catalyst and explained it on the basis of a selective catalytic effect. He also reported that the important products were the normal and isopropyl mercaptans and were produced with the ratio of approximately 65:35%. Mailhe(65) investigated the reactions between hydrogen sulfide and various hydrocarbons such as ethylene, propylene, butenes and pentenes at temperatures of up to 725°C and with silica gel as catalyst. He reported a complex mixture of products. The uses of several other catalysts for olefin-hydrogen sulfide addition reactions have been reported in the literature.

Wilke(98) observed that when cracked gasolines containing hydrogen sulfide are refined by treating with sulfuric acid, mercaptans are formed. Since some mercaptans of high molecular weight are important in the rubber industry for butadiene-styrene copolymerization, Schulze(83) formulated a synthesis method for the production of such mercaptans. This process incorporates the direct addition of hydrogen sulfide to olefinic hydrocarbons of petroleum origin in the presence of catalysts such as silica-alumina gel.

The addition reaction of hydrogen sulfide and other thiol compounds with aliphatic olefins, including propylene and isobutene, was studied by Ipatieff,(48) in order to analyze the structures of the products formed. The reactions were conducted between room temperature and 200°C without any catalyst. It was concluded that aliphatic mercaptans added to the ethylenic group contrary to Markownikoff's rule, whereas hydrogen sulfide added in accordance with the rule. Markownikoff's rule states that in the addition reaction of the aliphatic hydrocarbons, the more negative element or group of the addend, adds to the carbon atom having the lesser number of hydrogen atoms. The conclusion is exemplified below for the addition reaction of methyl mercaptan to propylene.

$$CH_3SH + CH_3CH = CH_2 \longrightarrow CH_3CH_2CH_2SCH_3 \quad \ldots (1)$$

It may be observed that the sulfur atom adds contrary to the rule and to the carbon atom having the larger number of hydrogen atoms.

The additions according to or contrary to Markownikoff's rule are generally termed as "normal addition" and "abnormal addition" respectively.

Ashworth(4) studied the addition of thiophenol to styrene and noted an effect of air and acceleration of the reaction by light. He suggested that the addition might proceed by a chain reaction. Burkhardt(10) suggested that free radicals may be involved in the addition reaction. Jones(50) employed peroxides to initiate thiol additions to olefins. Recently Ford(31) has reported the use of a peroxide catalyst together with metallic iron etc. for the butene hydrogen sulfide reaction.

Such addition reactions were also observed by Kharasch(52-54) and his group. They found that thioglycolic acid added to styrene and isobutene by a chain mechanism initiated by RS· radicals when catalyzed by peroxides. It was proposed that the mechanism of the so-called "peroxide-effect", which was first proposed for the addition of hydrogen bromide to olefins, applied in the mercaptan addition reaction also. The chain mechanism may be represented as follows:

$$RS\cdot + H_2C=CHR' \longrightarrow RSCH_2\dot{C}HR' \quad \ldots (2)$$

$$RSCH_2CHR' + RSH \longrightarrow RSCH_2CH_2R' + RS\cdot \ldots (3)$$

Vaughn(91-94) first observed that the addition of hydrogen sulfide or hydrogen bromide to olefinic bonds can easily be accomplished photochemically in both the liquid and the vapor phase. Radiation of a wavelength sufficiently short to dissociate hydrogen sulfide seemed to be the primary requisite for initiation of the addition reactions. Vaughn used a quartz mercury arc lamp as a radiation source and a quartz reaction vessel. It was also shown that light of a wavelength transmittable by Pyrex is effective in initiating the reaction if a small amount of photodissociable material such as acetone is present. The addition was found to be abnormal (i.e. contrary to Markownikoff's rule) and the sulfur of the sulfhydryl group added exclusively to the carbon atoms of the double bond having the larger number of hydrogen atoms. A free radical mechanism was proposed based on the preliminary dissociation of hydrogen sulfide. Arthur(5) investigated photochemical reaction between ethylene and hydrogen sulfide and reported similar conclusions.

The photo-initiated additions of mercaptans to olefins were studied by Sivertz(8,73) and his group. Azobisisobutyronitrile was used as a photosensitizer, and the reactions of butyl mercaptan with isoprene, styrene and 1-prentene were studied using benzene as a solvent. The study showed that the principal mechanism comprises an attack by the thiyl radical followed by transfer with mercaptan by the alkyl radical, as illustrated in Equations (2) and (3).

B. Radiation Effects

Even though there has been no study reported in literature on the influence of high energy radiation on the reactions of hydrogen sulfide and olefins, several investigations have been conducted on the radiolysis of olefins and of hydrogen sulfide. Some pertinent information can also be derived from studies in other addition reactions of olefins induced by radiation. These studies are briefly reviewed in this section.

1. Radiolysis of Hydrogen Sulfide

The effect of radiation on hydrogen sulfide has been studied mostly in the gas phase and with **X**-rays. Wourtzel(100) measured the decomposition and found -M/N to be 2.65 at 18°C. Mund(70) has proposed a mechanism for the decomposition reaction and compared it with the photochemical decomposition studied by Forbes.(30) Hydrogen sulfide absorbs light of wavelength 2800 A.°U.

Since the primary decomposition of H_2S results in the formation of H atoms and SH groups, some studies included radiolysis of mixtures of hydrogen and hydrogen sulfide to determine the secondary reactions, and are summarized by Lind.(60)

2. Radiolysis of Olefinic Hydrocarbons

Major work in the radiation chemistry of olefinic compounds has been in the field of polymerization of such compounds as ethylene.(43,60) The yields of hydrogen and other gaseous products from radiolysis of olefins are lower than those from the radiolysis of saturated hydrocarbons, while the overall radiation yield is higher for olefins if polymerization takes place.(20)

The determination of the free radical yields in olefins is difficult since they themselves act as scavengers and compete with any added solute for primary radicals. Further, many scavengers add to the double bonds of the olefins. However, it appears that the yields of free radicals in olefins are lower than those obtained for saturated hydrocarbons.(20) This is explained on the basis of the "protective" action of the double bond.(18) The latter, owing to the presence of π electrons, which can transfer and dissipate energy, could deactivate excited molecules which could otherwise dissociate into free radicals.

The radiation-induced polymerizations of vinyl monomers is usually interpreted in terms of free-radical reactions. However, some recent studies in polymerization of isobutylene by irradiation suggest that the reaction occurs by an ionic mechanism.(58) This suggestion, however, is rendered disputable by the observation that oxygen or benzoquinon, which are typical free radicals scavengers, inhibit the reaction.(18) An ionic process has also been suggested for the radiolysis of hexene-1 by Chang.(17) The conclusion was arrived at from the observation that 90% of the dimeric product was mono-olefinic. A low-yield of hydrogen gas and virtual absence of C-C fragmentation was reported.

3. Addition Reactions of Olefins

Fontijn studied the addition of n-butyl mercaptan to olefins induced by x-radiation and gamma radiation. The kinetics of the reaction was studied by dilatometric methods and a reaction mechanism was proposed. A similar work with several mercaptans and olefins was carried out by Aaraki(3) with cobalt-60 gamma radiation. Clingham(21) made a study of the free radical lifetime in the radiation-initiated reaction of n-butyl mercaptan and octene-1. In all the above-mentioned cases, it was proposed that the addition reaction proceeded by chain mechanism initiated by RS· radicals generated by the decomposition of the mercaptan under the effect of radiation.

The addition reaction of hydrogen bromide with ethylene induced by cobalt-60 gamma radiation was studied by Armstrong.(4) A commercial process for the production of ethyl bromide by the reaction of ethylene and hydrogen sulfide initiated by cobalt-60 gamma radiation has been reported by Harmer.(44)

Bray(15) studied the reactions of sulfur dioxide with ethylene, propylene, butene and other higher molecular weight olefinic compounds. The synthesis of polysulfones is described in detail with respect to the physical properties of the polymers and the kinetics of the reactions. Heiba(44) reported the addition of bromotrichloromethane to olefins. El-Abbady(27) and Roper(78) studied the addition reactions of silicon hydrides and triphenyl silane to olefins respectively. Lind(62) studied the irradiation of ethylene and hydrogen with alpha particles but found little or no hydrogenation.

4. Related Studies

Stacey(85) reported the use of x-radiation in the synthesis of divinyl sulfide and other sulfur compounds for mono- and di-substituted acetylenes and hydrogen sulfide. Lonthan(63) discussed a method for the production of unsaturated sulfides by irradiating a mixture of mercaptan and/or hydrogen sulfide with halogenated compounds.

Some studies have been conducted recently in the utilization of high energy radiation in petroleum processing.(38,40,63,71) The particular aspect of radiation sweetening of petroleum is discussed by Nevitt.(72) He concluded that the mercaptan conversion was reduced by the presence of aromatic compounds and increased by olefinic compounds in the petroleum stock. Grosmangin(38) has discussed the radiolysis of solution of some mercaptans.

The importance of sulfur compounds in biological sciences is well recognized.(16) The sulfhydryl group exhibits a protective effect in many biochemical systems, because of its own susceptibility to the attack by free radicals.(51,77) Thus, the protective effect of cystein is attributed to the presence of sulfhydryl group.(51) In the radiation treatment of foodstuffs, the production of hydrogen sulfide from thiols is an important consideration that deserves careful study.(89)

IV. EXPERIMENTAL METHODS

A. Radiation Source

All irradiations performed for this study used a cobalt-60 source for high energy radiation. This radioactive isotope of cobalt is produced when cobalt-59 is subjected to neutron bombardment. The decay scheme is as follows:

$$\mathrm{Co}^{60} \xrightarrow[(.059\ \mathrm{Mev})]{} \mathrm{Co}^{60} \xrightarrow[(0.31\ \mathrm{Mev})]{} \mathrm{Ni}^{60} \xrightarrow[(1.17\ \mathrm{Mev})]{} \mathrm{Ni}^{60} \xrightarrow[(1.33\ \mathrm{Mev})]{} \mathrm{Ni}^{60}$$

The two γ -photons of energy 1.17 and 1.33 Mev produced by each disintegration of cobalt-60 are mainly responsible for radiation effects. The rest of the energy is chiefly absorbed in the source itself. Cobalt-60 decays with a half life of 5.3 years.

The radiation source used in this study, was located at the Phoenix Radiation Facility of The University of Michigan. It was rated at approximately one kilocurie as of January 1961. The initial installation and operation of the source has been described elsewhere.(71) It consisted of 42 cobalt-60 aluminum-jacketed rods arranged in a cylindrical holder of 8-3/8" I.D. and 10-5/8" O.D. The individual rods were $\frac{1}{2}$ inch in diameter and 10 inches long. The holder was contained in a stainless steel capsule. An atmosphere of helium with a pressure slightly above the atmospheric pressure was maintained in the capsule. This arrangement prevented the corrosion of the aluminum-jacketed cobalt-60 rods which would be caused by direct immersion in water.

The source capsule was situated on an elevator mechanism in the source room. This room was 11 ft. long and 8 ft. wide, with 4 ft. walls of concrete and a 2 ft. concrete ceiling for shielding. The source was raised and lowered in the source room (cave) by the elevator, which was remotely operated. In order to enter the source room and place the samples to be irradiated, the source was lowered in a 16 ft. well (into about 12 ft. of water). When raised, the source entered into a perforated stainless steel annular cage. Interlocking mechanisms were provided to prevent accidental exposure.

The arrangement in the source room is shown in Figure 1 and 2. The samples to be irradiated may be placed in the center well (within the annulus of the perforated stainless steel cage) or outside of the source, depending upon the intensity of radiation desired.

B. Radiation Dosimetry

The dose-rates provided by the cobalt-60 gamma radiation source were measured by using the ferrous sulfate dosimeter. This method is based on the observation by Fricke(32,33) that an aqueous solution of ferrous ions is oxidized to ferric ions when subjected to ionizing radiation. Miller(69) and Weiss(97) developed this method for quantitative dosimetry for radiations of various types. Recently the American Society of Testing and Materials has accepted it as a tentative method of dosimetry.(7)

The presently accepted G-value (number of atoms reacting per 100 ev of absorbed energy) for this reaction is 15.5 ± 0.5.(18) The unit in current usage to express the absorbed dose is a 'rad' and is equal to 100 ergs or $6.25X10^{(13)}$ ev. of absorbed energy per gram. It differs from the unit roentgen, which is used to express the exposure dose, and is defined as the amount of radiation producing through ionization 1 electrostatic charge unit in .001293 g of air. It is equivalent to 88 ergs per gram of air, if W, the energy required to form an ion-pair in air, is assumed to be 34 ev.(18)

The concentration of the ferric ions produced in the dosimetry method is measured by determining the optical absorbance at a wavelength of 3050 A°U. The relation between the gamma dose and the optical absorption, as developed in the ASTM method,(7) is as follows:

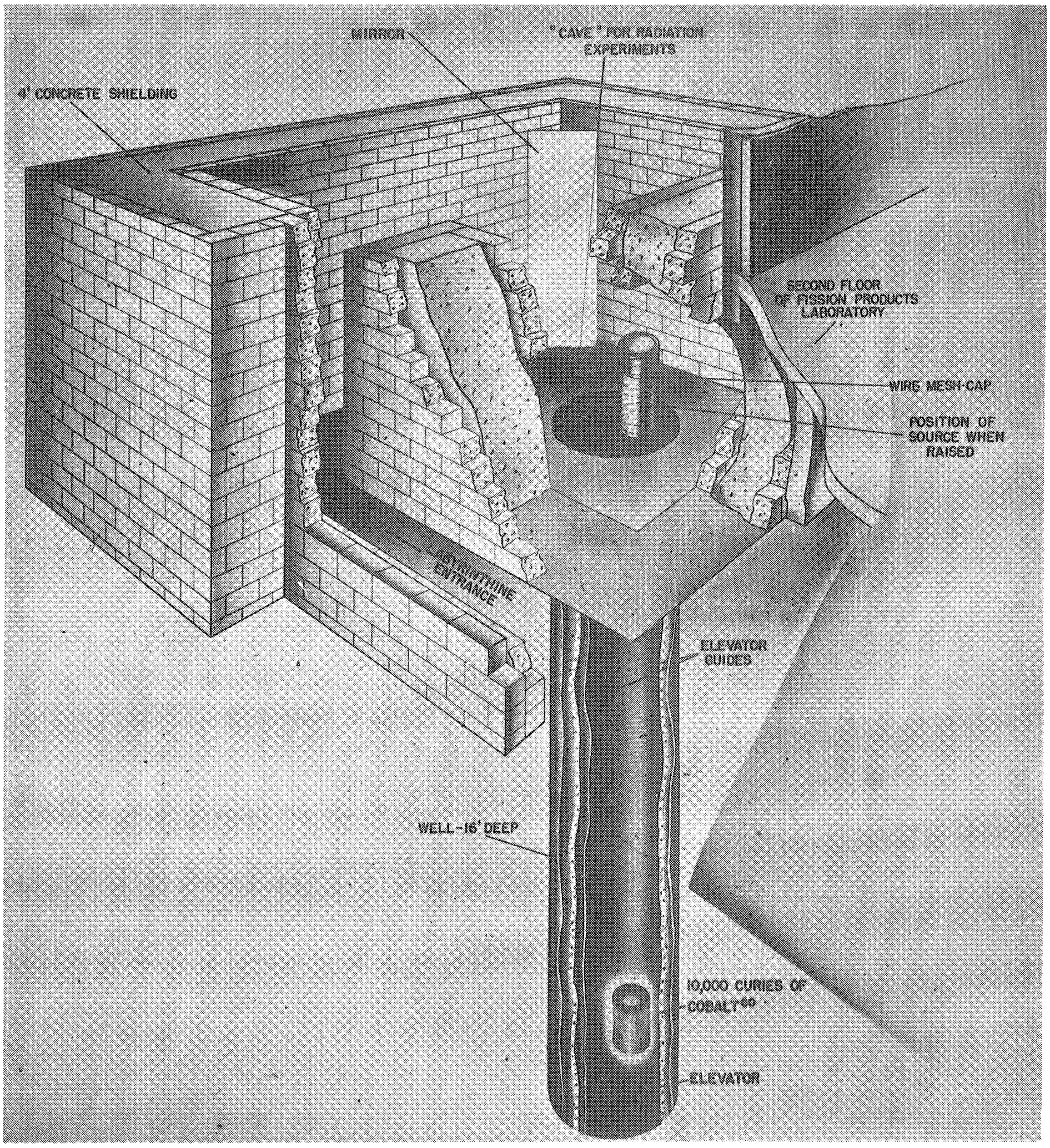


Figure 1. Perspective Cutaway View of the Cobalt-60 Gamma Radiation Facility. (NOTE: The name of the Fission Products Laboratory has been changed to the Phoenix Radiation Facility. The indicated 10,000 curies represents the nominal strength of the source as received.)

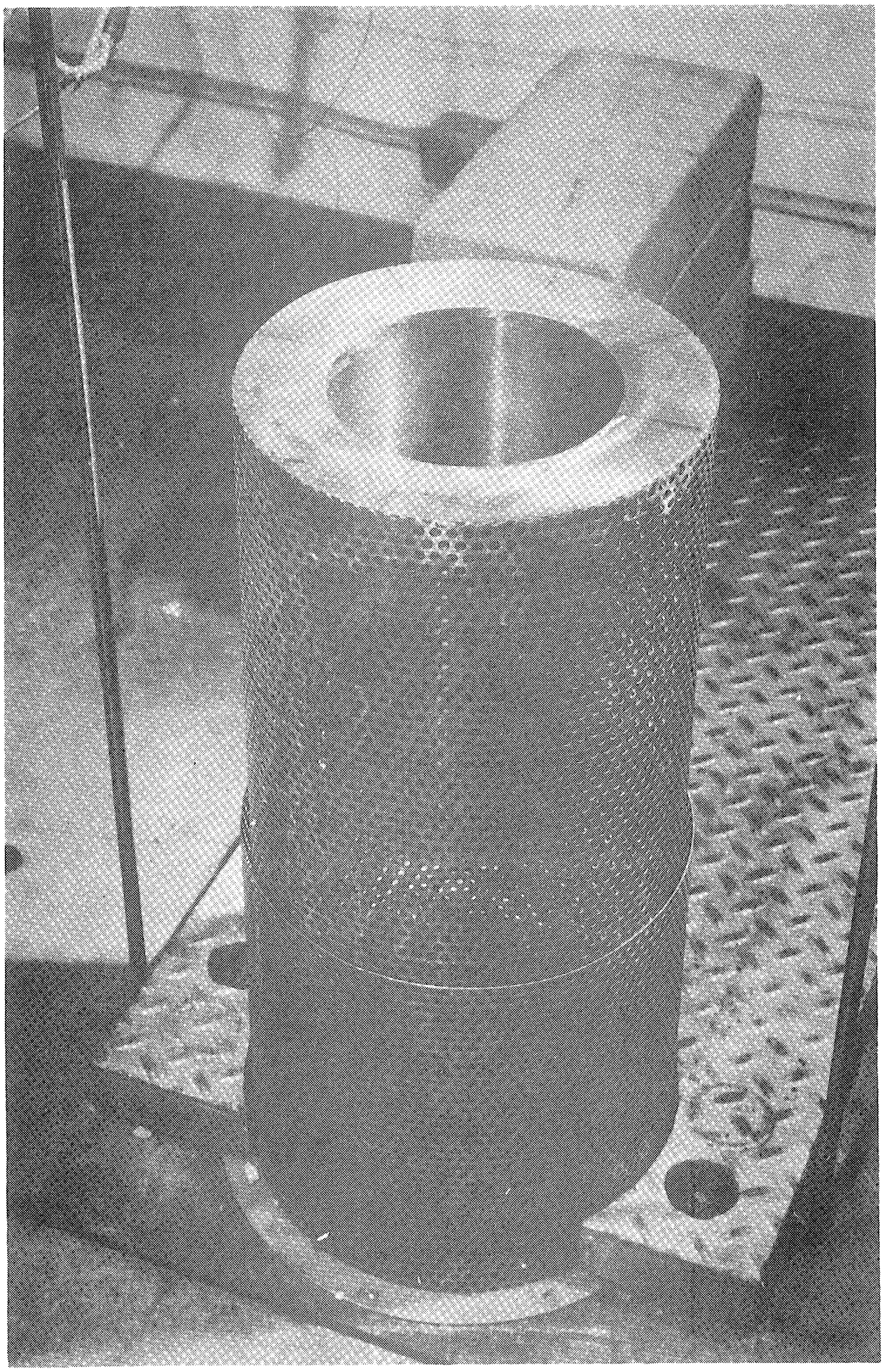


Figure 2. Phoenix Radiation Facility Cobalt-60 Gamma Radiation Source in the Cave.

$$\text{Dose (rads)} = \frac{\text{optical density X } 10^6 \text{ X } 944}{\text{G X extinction coefficient}} \qquad (4)$$

The extinction coefficient is defined as the optical density of a solution of concentration 1 mole/liter through a path length of 1 cm.

The ASTM method of dosimetry was used to determine the dose rates. This method is described below.

One hundred cc of a stock solution was prepared by dissolving reagent grade chemicals in double distilled water to obtain the following concentrations:

Ferrous ammonium sulfate	0.01 M.
Sodium Chloride	0.02 M.
Sulfuric acid	0.8 N.

With proper storage, the stock solution can be used for up to three months.

The stock solution was diluted 1:10 with 0.8 N H_2SO_4 and the reaction vessels were filled with it to an extent that duplicated the geometry of the experimental runs of the reaction under study. The solutions were irradiated for a specific and a measured amount of time. The exposure time was first estimated by the calibrations of the source that were available in the laboratory. After the irradiation and temperature equilibration of the solution with that of the instrument room, the optical densities of the solutions were measured on a Beckman DU spectrophotometer at a wavelength of 3050 A°U. and a slit width of 0.5 mm in quartz cells. A sample of unirradiated dosimetry solution was used as a blank. The temperature equilibrium and a knowledge of the temperature of measurement of optical density is necessary because the optical density of Fe^{+++} has a significant temperature coefficient.

Since the value of the extinction coefficient varies for different instruments, a calibration curve was made by Graikoski and Kempe(37) for the Beckman spectrophotometer at the Phoenix Radiation Facility. This was done by measuring the optical densities of a number of solutions containing varying amounts of Fe^{+++} at a wavelength of 3050 A°U. and a slit width of 0.5 mm. These solutions were made from a stock solution which was standardized by a reduction of Fe^{+++} to Fe^{++} in a Jones reductor and a subsequent oxidation of Fe^{++} by standardized permanganate solution. The permanganate solution was standardized with oxalic acid.

The average extinction coefficient was obtained by the method of least squares applied to the results was 2140.6 at 22°C. Using this value and G=15.5 in Equation (4), yields the value of dosefactor as 28300 at 22°C. Thus:

$$\text{Dose (rads)} = 28300 \times \text{Optical density} \qquad \ldots (5)$$

Since the extinction coefficient has a rather large temperature coefficient of 0.7 per cent per degree centigrade, a correction should be made if the optical density measurements are determined at a temperature other than 22°C referred to above.

$$\text{Dose (corrected)} = \frac{\text{Dose measured at } T_2}{1 + 0.007\,(T_2 - T_1)} \qquad \ldots (6)$$

where T_1 and T_2 are temperatures at which the calibration curve was made and at which the optical density measurements are made, respectively.

Some values of correction factors and dose factors used in this study are listed in Table VII (Appendix). The dose rates in the center well of the cobalt-60 source were mapped by Graikoski, et al.(37) and are shown in Figure 3. The dose rates obtained for various positions around the cobalt-60 source are shown in Table I and Figure 4. Since cobalt-60 decays in its radioactivity, the applicable dose rates for any time after the time of dosimetry were obtained either by new measurements or by employing the time decay law.

$$I = I_0 e^{-\lambda \theta} \qquad \ldots (7)$$

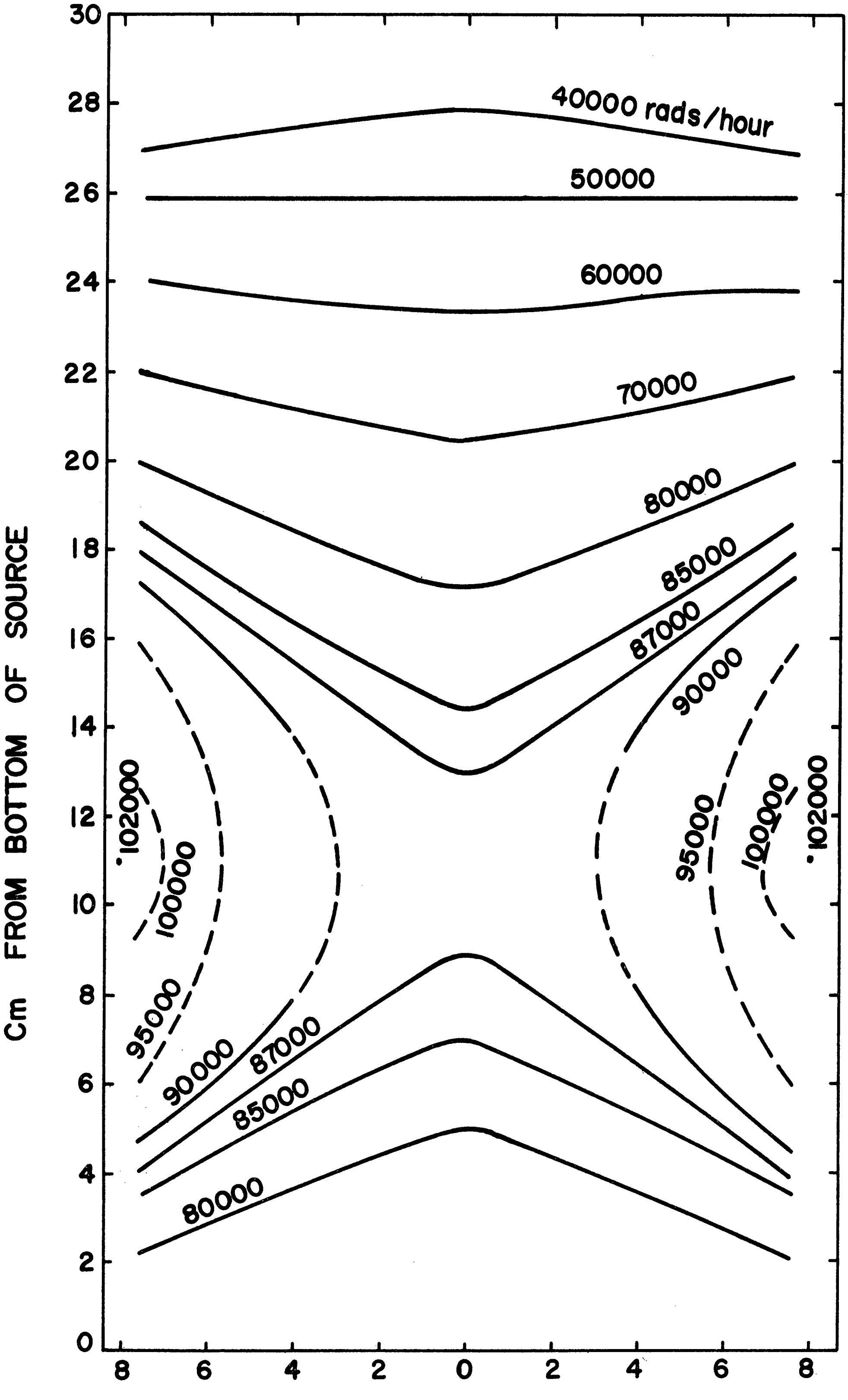


Figure 3. Phoenix Radiation Facility Cobalt-60 Gamma Radiation Source; Dose Rates in the Center Well of the Source

TABLE I

SUMMARY OF DOSIMETRY

Date	Position [*1] cm.	Dose Rate rads/min.	Dose Rate [*2] (normalized to 12-1-61) rads/ min.
4-1-61	cw	1570	1435
	5	833	763
	28	366	335
	37.5	216	198
	49.5	124	113.5
	63	75.7	69.3
12-1-61	46	134	134
	66	67.2	67.2
	96	30.8	30.8
	96	29.6	29.6
	110	21.7	21.7
8-24-62	75	42.9	46.8
	94	26.8	29.2

*1. Position cw stands for center well of the source. All other positions are measured from the outside edge of the cage.

*2. Decay-Correction factors (Table VIII) were used to normalize all data to 12-1-61.

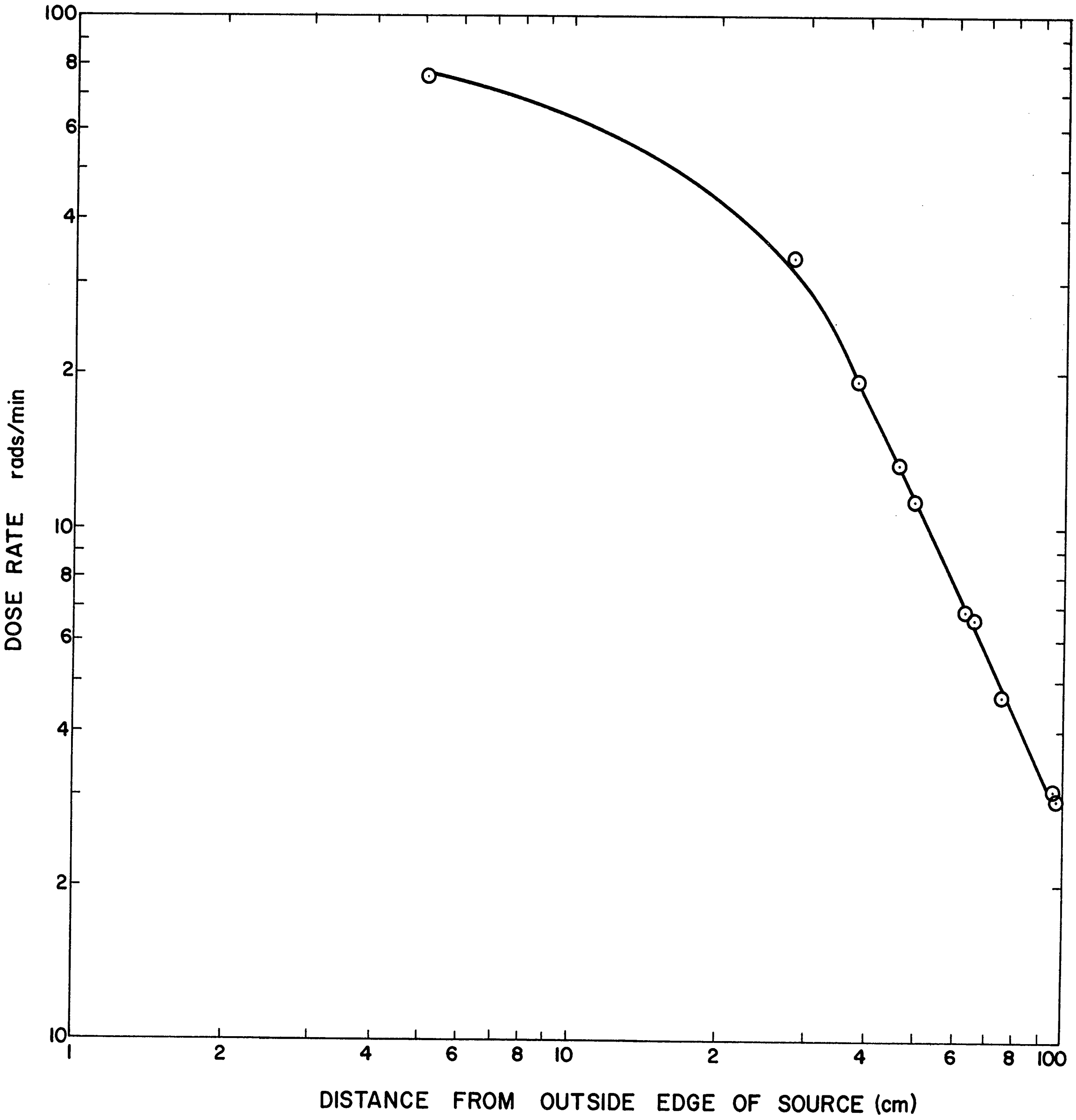


Figure 4. Phoenix Radiation Facility Cobalt-60 Gamma Radiation Source; Dose Rates Around the Source.

where I and I_0 are intensities at time θ and at time zero, respectively

θ = time interval in years

λ = average life = ln2/half life in years
= 0.693/5.3

Some decay correction factors are listed in Table VIII (Appendix).

C. Absorbed Dose

The absorbed dose measured by the ferrous sulfate dosimeter applies to systems where the major absorption of radiation occurs in water or systems similar to the dosimetry solution. For systems which may differ in absorption properties from water, a correction factor should be established.

The absorption of gamma radiation in matter is given by the following expression:

$$I = I_0 e^{-\mu x} \qquad (8)$$

Where I and I_0 are intensities of the final and original beam, x is the thickness of the absorbing material and μ is its linear absorption coefficient. The last term μ in turn is the sum of the photoelectric absorption coefficient τ, Compton scattering coefficient σ and pair production coefficient κ.

For cobalt-60 gamma radiation, the only significant method of dissipation of energy is by Compton scattering, particularly in a medium containing light elements. In such a case, the absorbed dose is directly proportional to the number of electrons per gram of the substance.

The number of orbital electrons per gram of common elements like H, C, O and S are 6.0, 3.02, 3.01 and 3.0 X 10^{23} respectively.(18) The number of electrons per gram of water, propylene and hydrogen sulfide are 3.33, 3.44, and 3.17 respectively.

For an equimolar mixture of propylene and hydrogen sulfide, the correction factor is less than 1%. However, as the weight fractions of hydrogen in the mixture increase, the correction factors become more substantial.

D. Reaction Studies

The radiation induced reactions of hydrogen sulfide with four different olefins were studied. These olefins were propylene, butene-1, butene-2 and isobutene. The effects of the time of irradiation and of the total dose were used to determine the G-values and the rates of the reactions. Analytical methods were developed to establish the distribution of the reaction products.

For the propylene-hydrogen sulfide system the effects of such variables as dose-rate, concentration and temperature were also investigated. Dose-rate was varied between approximately 10^3 to 10^5 rads/hr. ($6.25 X 10^{16}$ to $6.25 X 10^{18}$ ev/hr.). Since no solvent was used, only the relative amounts of the two reactants in the reaction mixture were varied. The temperature was varied between -78^o to $-25^{o}C$. The limitations of the glass reactors fixed the upper limit on temperature.

All reactions were carried out in the condensed phase in glass reactors. The reactors were sealed with reactants in the liquid phase under the vapor pressure of the reactant mixture. The pressure was below the atmospheric pressure for experiments conducted at -78^oC and -65^oC before and after irradiation. At -25^oC, however, the vapor pressures of hydrogen sulfide and propylene are approximately 5 and 2.5 atmospheres respectively. In this case heavy-walled glass vials that would withstand superatmospheric pressures were used as reactors.

In all experiments observations were made to detect the precipitation of any solid products. No such formation of a precipitate was noticeable. Control runs performed without any irradiation indicated that the addition reaction did not occur under conditions similar to those used for the study.

1. Materials

The olefins and hydrogen sulfide were obtained commercially from Matheson Gas Co. The C. P. grade propylene, butene-1, butene-2 and isobutene had a minimum purity of 99 mole %. The hydrogen sulfide was of pure grade and was received as of 99.9 mole % purity. The main impurities in the olefinic hydrocarbons were the corresponding saturated hydrocarbons. The information about purities of the gases as provided by the supplier was checked by chromatographic analysis.

Since the loading procedure consisted of distillation and condensation of the reactants into the reactors, and since further degassing steps as described in the following section were employed, no separate methods of purification were thought to be necessary.

The samples of various mercaptans and sulfides used as chromatographic standards were obtained from Eastman Kodak Co. These samples were analyzed on a Fisher-Gulf Partitioner. Helium was used as a carrier gas and was obtained from Air Reduction Co. The main impurities were found to be the corresponding isomers and were accounted for in the preparation of the standards. The chemicals used for dosimetry were of the reagent grade. Double-distilled water as prepared in the labortory was used for the dosimetry solution and considered of adequate purity. The addition of sodium chloride to the dosimetry solution eliminates the need for high-purity water.

2. Experiment Equipment

All experimental data were taken in small batch reactors. The reactors used for experiments at temperatures of -78°C and -65°C were constructed from standard Pyrex tubing and Pyrex vaccum stopcocks. The lower part of such a reactor consisted of a 3/4" O. D., 10" long tube which was sealed and rounded at the bottom and of a 24/40 plug type outer joint, to which a 7 mm. vacuum stopcock was attached by glass-blowing techniques. The top and the bottom parts were sealed together by Dow Corning high vacuum silicone grease.

The experiments conducted at -25°C, were superatmospheric pressures were encountered, were carried out in reactors which were blown from heavy-walled Pyrex tubing. When properly sealed they were expected to stand pressures up to about ten atmospheres. These glass reactors have been described by Bray(15) Such a reactor was made out of a 10" long, 3/4" O.D. tube with a wall thickness of 1/8". The bottom part of the tube was sealed and rounded. The top part was constricted and a 2" section of 7 mm. standard Pyrex tubing was attached to the constricted neck to facilitate connection to the gas loading manifold. The reactors were properly annealed to remove any thermal stresses remaining after construction. After the loading of the reactants the reactors were flame-sealed at the constricted end.

A gas loading manifold was constructed to facilitate the loading of the glass reactors under vacuum. A schematic diagram of this system is shown in Figure 5. Pyrex tubing and Pyrex high vacuum stopcocks were used in the construction of the manifold. Various outlets on the manifold were used to connect the reactors and the reactant gas cylinders. A standard Welch "Duo-Seal" pump capable of producing less than 100 microns of mercury pressure was used to evacuate the system and was connected to the manifold through a liquid nitrogen cold trap. All connections were made with heavy-walled vacuum tygon tubing, sealed to the glass tubing outlets on the manifold with Dow Corning high vacuum silicone grease. An Ashcroft "Dura-gauge" was connected to the manifold and indicated vacuum in inches of mercury and pressure up to 30 psig. This was mainly used to detect any pressure build-up in the glass line during the operations in the loading of the reactors.

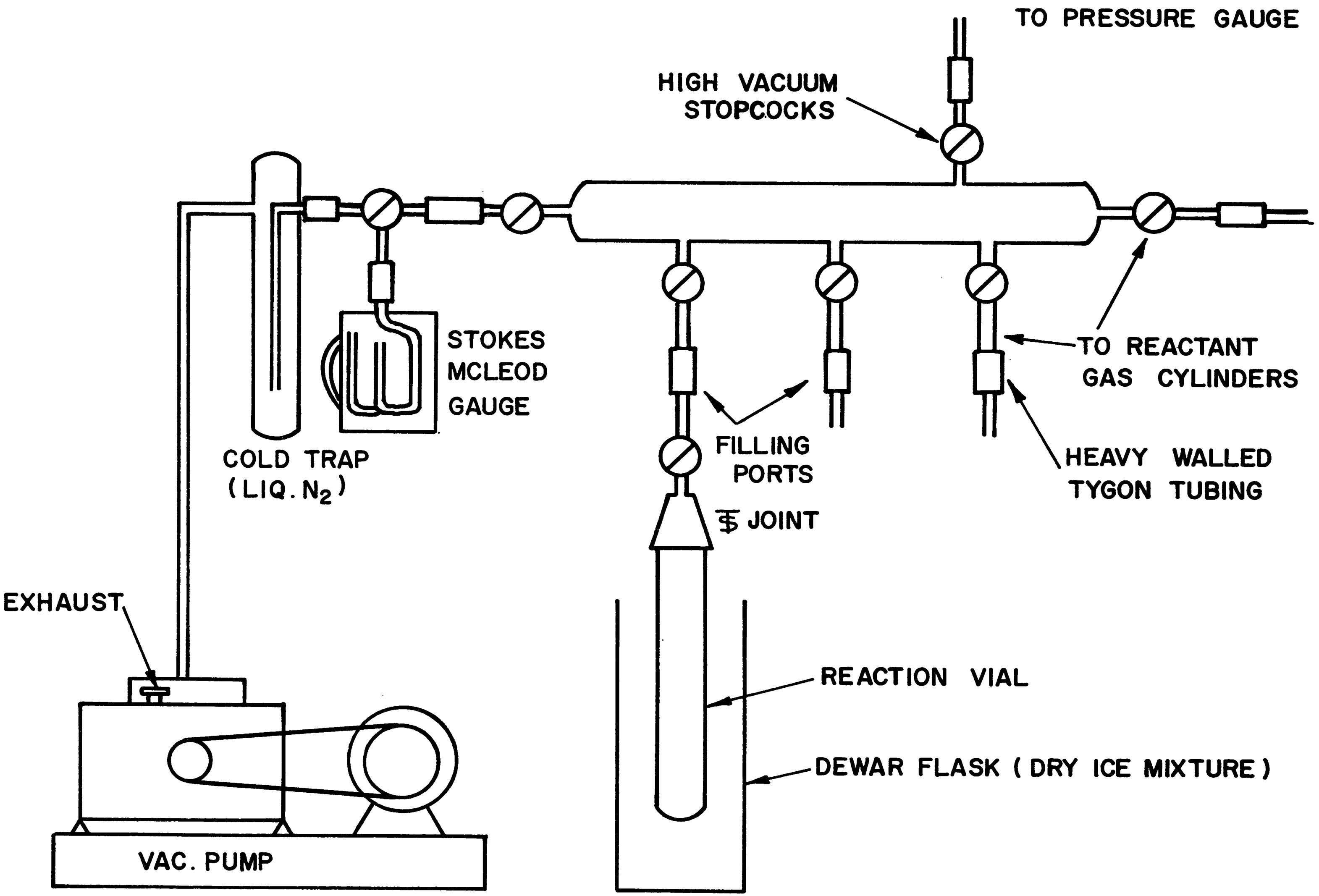


Figure 5. Schematic Diagram of the Reactant Loading System.

A Fisher-Gulf Partitioner model 11-130 was used for the chromatographic analysis. Optical density measurements for the radiation dosimetry were made on a Beckman DU spectrophotometer with a matched set of four quartz cells.

3. Experimental Procedure

In radiation chemistry it is known that small amounts of impurities have very significant effects on the course of a chemical reaction. Small amounts of oxygen present in a system can inhibit a reaction, particularly if the initiation of the reaction is through a free radical mechanism. Owing to this, particular care was taken to employ clean glass reactors and to eliminate oxygen from the system.

The construction of a gas loading manifold has been described. This system permitted the loading of two reactors at any one time. The loading procedure is described below.

After a reactor was connected to a manifold, the whole system was evacuated. Before use the system was checked for any leaks. The major leaks were located by leaving various parts of the system under vacuum overnight and checking for any pressure build-up on the following day. Any other leaks were checked by the use of a McLeod gauge. Immediately before use the system was flushed with the reactant gases before loading. Besides flushing the system, this also served the purpose of venting the gases from the top parts of the cylinders, where impurities such as noncondensable gases are more likely to be present. Throughout the loading operation the vacuum pump was left running even though the stopcock connecting the pump to the cylinder had to be shut off while loading the reactant gases. A liquid nitrogen cold trap protected the pump from harmful vapors.

After evacuation of a reactor it was immersed in a low temperature bath. The low temperature bath was made by cooling a 60-40% mixture of chloroform and carbon tetrachloride with dry ice and provided a temperature of -78°C. A predetermined amount of reactant gases, measured by volume, were condensed in the reactor from the gas cylinders. The olefin was loaded first, and the whole system, except for the reactor, was re-evacuated before the loading of hydrogen sulfide.

After the completion of the loading operation the reactor was immersed in a liquid nitrogen bath to freeze the reactant gases. The reactor was evacuated for one minute, and the stopcock connecting it to the manifold was shut off. The reactant gases were allowed to liquefy by pulling the reactor out of the cold bath; then they were refrozen and re-evacuated. This process of degassing was repeated three times and was expected to eliminate oxygen and other non-condensable gases. However, it did not result in any significant loss of the reactant gases.

For the experiments conducted with standard wall Pyrex reactors the stopcocks on the reactor itself and the one connecting it to the maniforld were closed, and the reactor was detached from the system. It was kept immersed in the dry ice bath until the time of irradiation. This prevented any pressure build-up in the reactor that might blow apart the top and the bottom parts of the reactor.

For the experiments carried out in the heavy-walled glass reactors the procedure for disconnecting the reactor was different. After the degassing operation the reactants were kept frozen by keeping the reactor immersed in a liquid nitrogen bath, and the connecting stopcock on the manifold was closed. The reactor was then detached by flam-sealing of the constricte end. A natural gas-oxygen torch was used for this purpose.

Before irradiation the reactor was placed in an appropriate constant temperature bath. The reactions carried out at -78°C were performed in the dry ice-chloroform-carbon tetrachloride bath already described. Equal amounts of dry ice and carbon tetrachloride and chloroform mixture in a Dewar flask (wide mouth type, capacity one qt.) made the constant temperature bath fluid enough to give good heat exchange properties. At the same time, when properly corked, the low temperature was maintained for up to 12 hours.

The irradiation was performed almost immediately after the reactor was loaded. It was placed at a specific distance from the cobalt-60 radiation source. The position was predetermined, and the determinations of dose-rates at various distances and with geometrical arrangements similar to that of the reactor were made by ferrous sulfate dosimetry. For all irradiations the vertical midplane of the reaction mixture was centered around the vertical midplane of the source. Since the total height of the liquid mixture was less than 2 inches, and since, in most cases, the reactor was placed at least 15 inches away from the source, the volume of the reaction mixture was expected to get a fairly homogeneous exposure to the field for a specific duration of time.

After irradiation the glass reactor was opened immediately, and the contents were poured into a small beaker. The heavy-walled reactors had to be broken open. This was done after freezing the reaction mixture with a liquid nitrogen bath. The break was made at the tip by touching a hot glass rod to a scratch made with a glass knife.

While the unreacted gases evaporated from the reaction mixture, the reactor was rinsed with a measured amount of toluene, which was introduced by a syringe. This was added to the beaker, and the contents were transferred in a 2 oz. glass bottle with vapor-tight polythene screw-cap. The weight of the product was determined after all the gases had evaporated, and the bottle was then stored in a refrigerator ($< 0^{o}C$) until the time of analysis.

The addition of toluene served other purposes besides that of rinsing the reactor. It was expected to reduce the loss of more volatile components of the product while in storage. The dilution of the product facilitated the chromatographic analysis, and the known amount of toluene acted as an internal standard. Toluene was chosen rather than benzene, because the latter interfered in the chromatographic analysis by having similar retention time to that of the products.

4. Analytical Methods

The determination of mercaptans and sulfides is usually conducted by titrimetric methods employing either iodine or silver nitrate as reagents.(48) However, a number of papers have recently appeared, suggesting the use of gas-liquid chromatography for analysis of volatile organic sulfur compounds.(1,79) Ryce and Bryce (79) have suggested the use of tri-o-tolyl phosphate as the liquid phase in a partition-elution column. Adams(1) has suggested the use of solvents of the alkyl aryl polyether alcohol type, such as the compound with the trade name of Triton X-305.

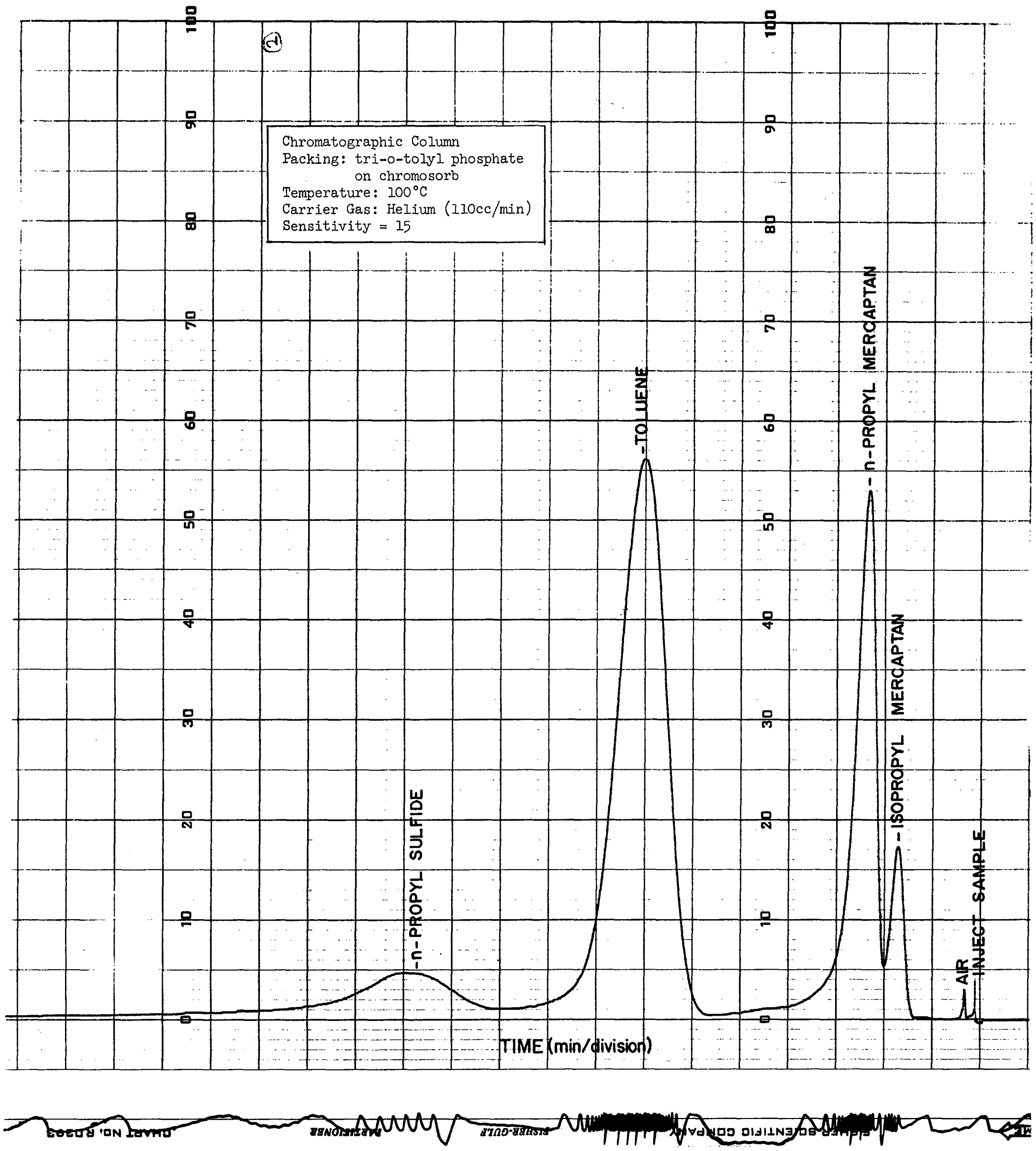
For the present study the chromatographic method was used in general and was supplemented by other techniques, such as distillation and mass spectrometric analysis.

For the chromatographic method various materials for stationary phase and other variables were investigated to determine a suitable analytical procedure. Some product samples and some standard samples of the expected products, including mercaptans, sulfides, disulfides and the isomeric compounds, were used for this determination. All the analyses were made on the Fisher-Gulf chromatography unit (model 11-130). On this unit the temperature of analysis could be controlled between 35 and 160°C. The products were quantitatively analyzed by using a thermal conductivity cell and by using helium as a carrier gas. The flow rates were measured by using a rotameter which was calibrated by a soap-bubble tower.

The materials, tri-o-tolyl phosphate, silicone oil-550 and Tide, a commercial detergent, were tried as stationary phases on a Chromosorb support. The columns were constructed out of $\frac{1}{4}$" copper or steel tubing, and the lengths were varied between 4 and 12 feet. The coating of the stationary phase on the support and the construction of the columns were carried out by using standard procedures. Approximately 4 grams of coated support material (about 30 weight % of the liquid phase) were used per foot of column length. The temperature was varied between 80°C and 120°C, and the flowrate was varied between 30 and 120 cc/minute at approximately 22°C and atmospheric pressure. The inlet pressure of helium was maintained at 20 psig. by using a two stage regulator.

The best separation for propylene-hydrogen sulfide reaction products was obtained using a 7 ft. stainless steel, tri-o-tolyl phosphate column at 100°C. The optimum flowrate of helium was found to be 110 cc/minute. With silicone oil the propyl sulfide peak showed a pronounced trailing effect. The reproducibility was not very good with Tide, and owing to the corrosion problems copper was not considered to be a good column construction material. For separation of butyl mercaptans and sulfides the same system was used with a temperature of 120°C. The retention times of various sulfur compounds are noted in Table X (Appendix), and typical chromatograms are shown in Figures 6 and 7.

For quantitative analysis of the reaction products the method outlined above was standardized and calibration was made by prepared standard samples. These standard samples were mixtures of various compounds which were expected in the reaction products. The compositions of these standards and the analysis obtained are shown in Table XI (Appendix). All correlations were made by using weight fractions of all the compounds in the samples.



Chromatographic Column
Packing: tri-o-tolyl phosphate
on chromosorb
Temperature: 100°C
Carrier Gas: Helium (110cc/min)
Sensitivity = 15

Figure 6. Chromatogram of Propyl Mercaptan, Toluene and Propyl Sulfide.

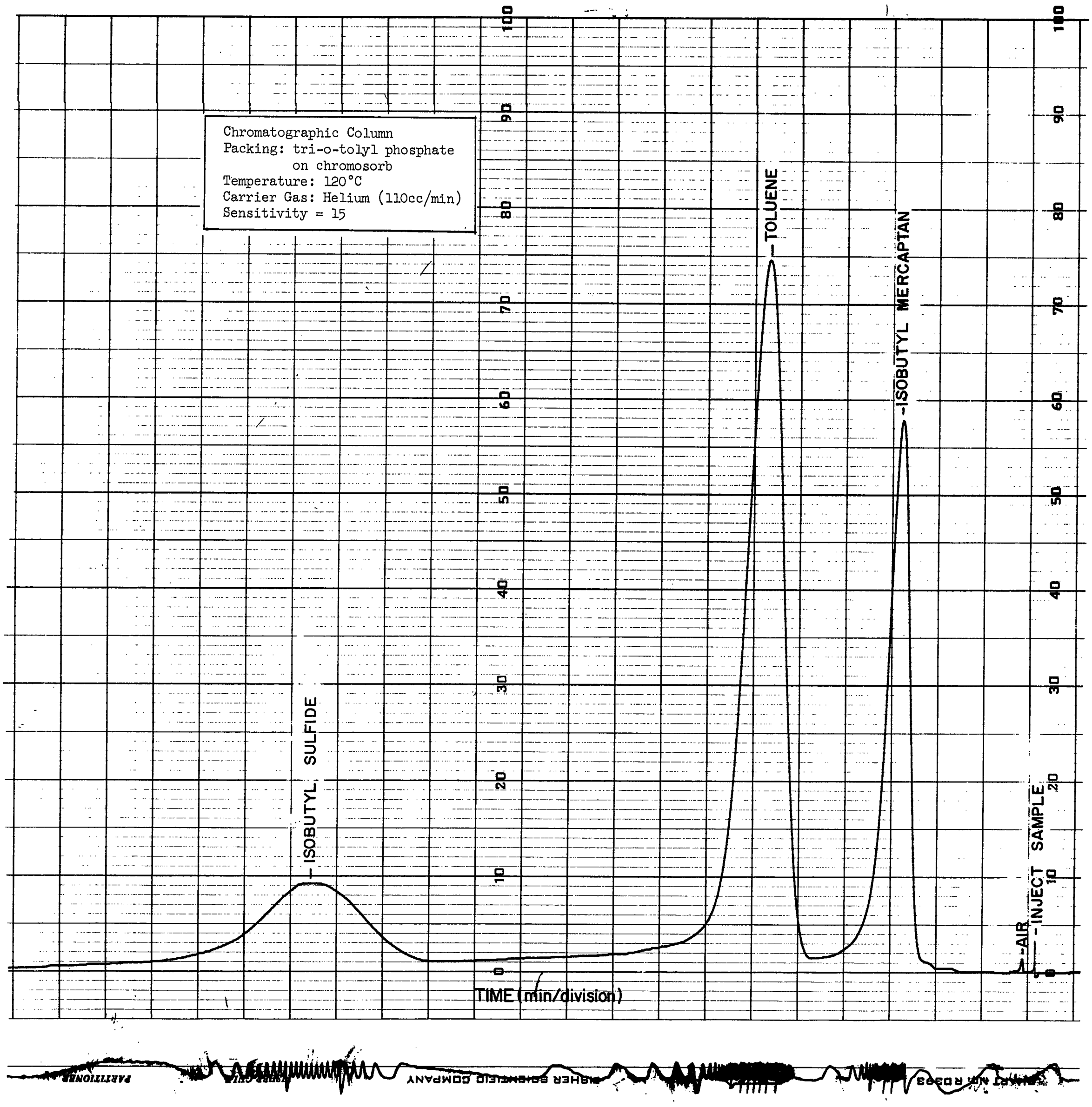


Figure 7. Chromatogram of Isobutyl Mercaptan, Toluene and Isobutyl Sulfide.

Besides the chromatographic method some samples were analyzed by distillation, and the boiling points of the components were determined for specific identification of major products. A semi-micro distillation column was built for this purpose. In addition, since the mercaptans form sodium salts when treated with sodium hydroxide, the method was used to estimate the amounts of mercaptans and sulfides formed in some initial studies. The mass spectometric analysis was also employed in initial studies to detect the formation of other products. An infrared spectrum was obtained for an irradiated sample of propylene and hydrogen sulfide and is shown in Figure 8 together with the spectrum of a sample of propyl mercaptan. The spectrum was obtained using a Baird Associates infrared spectrophotometer with a sodium chloride prism. Benzene was used as a solvent.

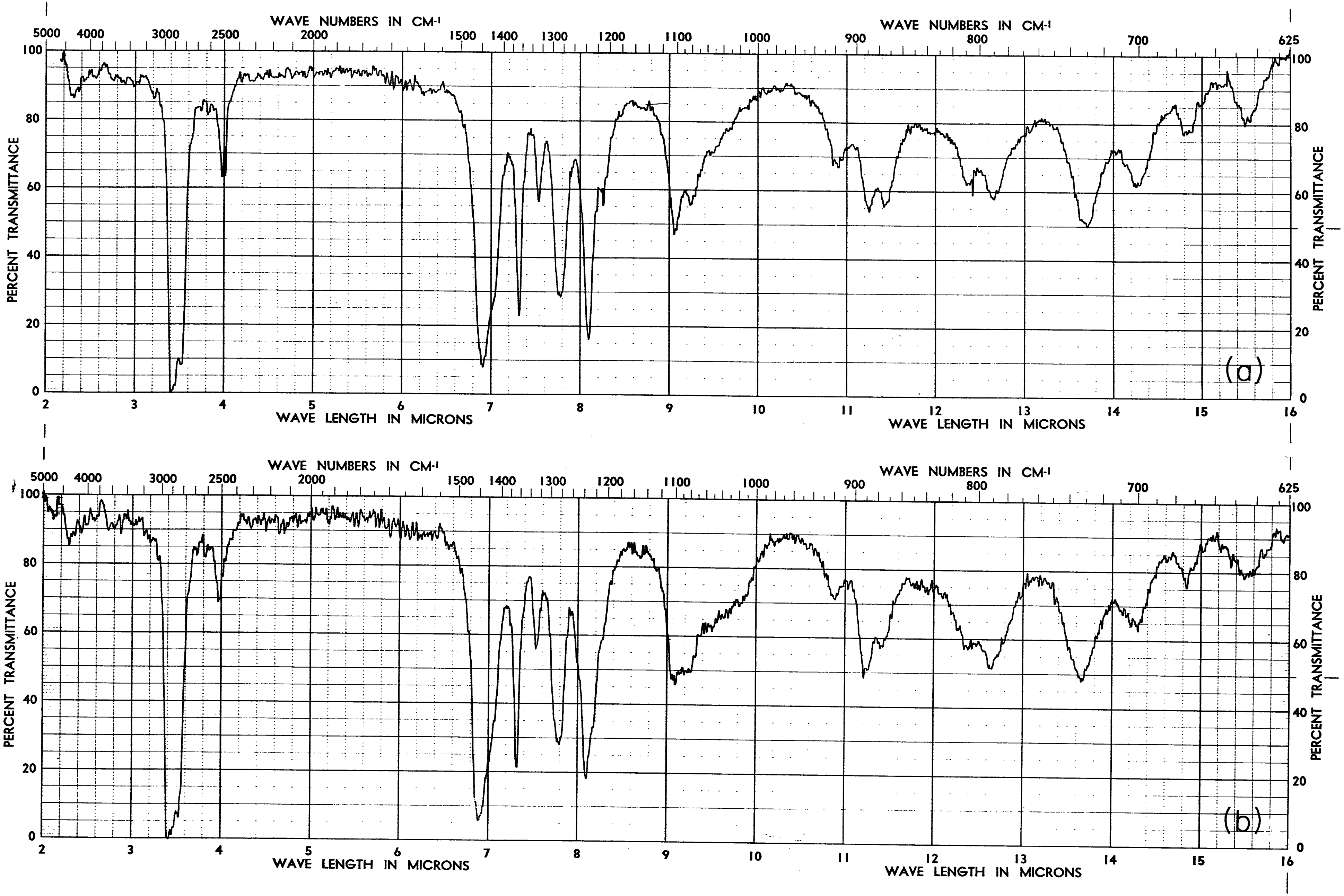


Figure 8. Infrared Spectrum; (a) Propylene-Hydrogen Sulfide Reaction Product, (b) Commercial n-Propyl Mercaptan.

V. EXPERIMENTAL RESULTS

A. Preliminary Investigations; Propylene-Hydrogen Sulfide

A number of experimental runs were conducted with propylene and hydrogen sulfide to establish the range of variables to be studied for the final experimental program. For these investigations technical grade hydrogen sulfide and C.P. grade propylene were used. The purities of these materials were considered sufficient for the preliminary studies. The experimental conditions used and the calculated results obtained are shown in Table XII (Appendix). The nature of the products formed and their amounts were determined by chromatographic analysis. These data were used to calculate the per cent conversion and the G-value, both of which are based on the necessary stoichiometric amount of hydrogen sulfide.

The investigation showed that in the absence of radiation no reaction takes place. However, radiation showed a definite effect, and high G-values for the reaction were obtained. Run number 17, which was conducted with the presence of oxygen, showed a low yield. The observation that oxygen inhibits the reaction was also evident in further experimental studies when proper evacuation was not obtained because of a faulty vacuum system.

Owing to the limitations of observations with batch reactors, it was difficult to observe any inhibition period. The data indicated that at high intensities the reaction is extremely rapid and inhibition period, if any, may be masked. Some low intensity runs did show S-shaped curves for time-composition diagrams. The reaction rates levelled off at about 40% conversion of hydrogen sulfide.

The chromatographic analysis showed two major products; namely, the normal propyl mercaptan and the normal propyl sulfide. The separation method with sodium hydroxide for the mercaptan and the sulfide, as suggested by Vaughn,(92) produced results similar to those produced by the chromatographic technique. However, this method was crude and too time-consuming for the kinetic study.

The infrared spectrum for the product of irradiation of equimolar quantities of propylene and hydrogen sulfide at a temperature of -78°C shown in Figure 8, together with an infrared spectrum for commercially obtained propyl mercaptan sample, verifies the presence of the mercaptan in the reaction product by the -SH stretching vibration at 2560 cm^{-1}. The mass spectrometric analysis was also used to verify the structures of the identified products and to determine any minor fractions which may not have been observed by the chromatographic technique. The minor fractions indicated by this analysis were isopropyl and ethylisobutyl sulfides and disulfides. The total disulfides constituted less than 0.5 mole per cent of the total products.

As noted earlier, the experimental runs conducted in this part of the study were made with technical grade of hydrogen sulfide. It may be observed from Table XII that the conversion and composition data are erratic and this may be attributed to the effects of any impurities present in the system or in the reactant gases. Also, most of the runs were carried out for extended periods of time and hence the data were not considered to be suitable for kinetic analysis. Hence, further investigation on the propylene-hydrogen sulfide reaction were carried out with pure grade of hydrogen sulfide to study the kinetics of the reaction.

B. Further Investigation of the Propylene-Hydrogen Sulfide Reaction

The propylene-hydrogen sulfide reaction was studied further to investigate the kinetics of the reaction. This system was chosen over the other systems consisting of higher molecular weight hydrocarbons because the chromatographic method was well suited for quantitative determination of the reaction products. For this investigation hydrogen sulfide of high purity (Pure grade with 99.9 mole per cent purity) was used as opposed to the technical grade of hydrogen sulfide used for preliminary investigation.

1. Stoichiometry of the Reaction

The addition reaction of propylene and hydrogen sulfide is represented by the following equation,

$$C_3H_6 + H_2S \rightleftharpoons C_3H_7SH \qquad \ldots (9)$$

The propyl mercaptan formed in the forward reaction may decompose to yield the reactants by a reverse reaction, which has been shown to occur in the thermally initiated reaction studied by Duffey,(26) Barr,(9) and Taylor.(91) The mercaptan can also react further and add to another molecule of propylene to yield propyl sulfide.

$$C_3H_7SH + C_3H_6 \rightleftharpoons C_3H_7SC_3H_7 \qquad \ldots (10)$$

As indicated in the previous section, the major products of the reaction were found to be the above mentioned propyl mercaptan and propyl sulfide. It was found, however, that propyl sulfide was not formed at low conversions of propylene and hydrogen sulfide, indicating that the sulfide is formed via the two consecutive reactions (Equations (9)(10)) rather than by some other radiation-induced reaction.

It should be noted that the above equations indicate only the overall reaction. However, the reactions were found to be of the chain type, and the mechanism is discussed in the next chapter.

2. Formulation of the Rate Equation

The product distribution as obtained by the chromatographic analysis can be readily converted into moles of propyl mercaptan and propyl sulfide formed. Since the reaction was conducted in the liquid phase, and since the conversion values were low (up to about thirty per cent reaction) the volume of the reaction mixture may be assumed to be constant. The formation of the products can then be expressed in terms of concentrations in the reaction mixture. All such concentrations are expressed in terms of moles/liter.

All conversions and G-values reported in the following sections are based on the consumption of hydrogen sulfide which was chosen as the key component. The disappearance of the hydrogen sulfide is equivalent to the sum of the formation of propyl mercaptan and propyl sulfide. The overall reaction rates were correlated by kinetic expressions formulated as follows. The rate of disappearance of hydrogen sulfide according to (Equation (9) is given by the following equation.

$$-\frac{d\left[H_2S\right]}{dt} = k\left[C_3H_6\right]\left[H_2S\right] - k_r\left[C_3H_7SH\right] \qquad \ldots (11)$$

where k and k_r are reaction rate constants for the forward and reverse reactions represented in (Equation (9)).

Using the following notations,

C_A, C_B, C_C and C_D...concentrations of H_2S, C_3H_6, C_3H_7SH and $C_3H_7SC_3H_7$ respectively (moles/liter)

C_{AO} and C_{BO}.........initial concentrations of H_2S and C_3H_6 respectively (moles/liter)

X_A..........H_2S reacted (moles/liter)

(Equation (11) may be rewritten as,

$$\frac{dX_A}{dt} = kC_AC_B - k_rC_C \qquad \ldots (12)$$

In order to express the concentrations C_A, C_B and C_C in terms of the known initial concentrations C_{AO} and C_{BO} and the reaction variable X_A, and to integrate Equation (12), certain simplifying assumptions were made. The major part of the experimental data was taken at low intensities and the conversion of hydrogen sulfide was less than thirty per cent of the initial charge. The amount of propyl sulfide formed was less than ten per cent of the total products. In such a case, it may be noted that the concentration terms C_A and C_B have much larger values than the concentration term C_C which in turn is larger than C_D. Thus, neglecting C_D, the concentrations C_A, C_B and C_C are given by $C_A = C_{AO}-X_A$, $C_B = C_{BO}-X_A$ and $C_C = X_A$. The total concentration of the reacting species is given by $C_{AO}+C_{BO}-X_A$. Rate Equation (12) may be written as follows,

$$\frac{dX_A}{dt} = k(C_{AO}-X_A)(C_{BO}-X_A) - k_r(X_A) \quad \ldots (13)$$

$$= k\left\{(C_{AO}-X_A)(C_{BO}-X_A) - \frac{k_r}{k}(X_A)\right\} \quad \ldots (14)$$

Denoting $k_r/k = \lambda$,

$$\frac{dX_A}{dt} = k\left\{(C_{AO}-X_A)(C_{BO}-X_A) - \lambda(X_A)\right\} \quad \ldots (15)$$

After separation of variables, the equation may be integrated.

$$\int_0^t dt = \frac{1}{k}\int_0^{X_A} \frac{dX_A}{C_{AO}C_{BO} - (C_{AO}+C_{BO}+\lambda)X_A + X_A^2} \quad \ldots (16)$$

Denoting $p = C_{AO}C_{BO}$ and $r = (C_{AO}+C_{BO}+\lambda)$

$$\int_0^t dt = \frac{1}{k}\int_0^{X_A} \frac{dX_A}{p - rX_A + X_A^2} \quad \ldots (17)$$

Integration with $q = 4P - r^2 = 4C_{AO}C_{BO} - (C_{AO} + C_{BO} + \lambda)^2$

$$t = \frac{1}{k\sqrt{-q}} \ln\left[\left\{\frac{2X_A - r - \sqrt{-q}}{2X_A - r + \sqrt{-q}}\right\} \left\{\frac{-r + \sqrt{-q}}{-r - \sqrt{-q}}\right\}\right] \quad \ldots (18)$$

Or in terms of the original symbols,

$$t = \frac{1}{k\sqrt{\left\{4C_{AO}C_{BO} - (C_{AO} + C_{BO} + \lambda)^2\right\}}} \ln\left[\frac{2X_A - (C_{AO} + C_{BO} + \lambda) - \sqrt{\left\{4C_{AO}C_{BO} - (C_{AO} + C_{BO} + \lambda)^2\right\}}}{2X_A - (C_{AO} + C_{BO} + \lambda) + \sqrt{\left\{4C_{AO}C_{BO} - (C_{AO} + C_{BO} + \lambda)^2\right\}}}\right.$$

$$\left.\frac{-(C_{AO} + C_{BO} + \lambda) + \sqrt{\left\{4C_{AO}C_{BO} - (C_{AO} + C_{BO} + \lambda)^2\right\}}}{-(C_{AO} + C_{BO} + \lambda) - \sqrt{\left\{4C_{AO}C_{BO} - (C_{AO} + C_{BO} + \lambda)^2\right\}}}\right] \quad \ldots (19)$$

For solution of Equation (18) or (19) the values of concentrations C_{AO}, C_{BO} and X_A and the reaction time t are known from experimental data. Since the value of λ which is the ratio of the reverse and the forward reaction rates, is not known, the experimental data may be fitted only after assuming a value of λ, to calculate the reaction rate constant.

3. Correlation of the Data

The experimental data obtained are tabulated in Tables XIII through XVII. The radiation intensity was varied between 30.6 and 1570 rads per minute. The data obtained at high intensities (365 to 1570 rads/min) and at low intensities (30.6 to 116.6 rads/min) are reported in Tables XIII and XIV respectively. The dark runs and long time irradiations are listed in Table XV. All the runs listed in Tables XIII through Table XV were carried out at -78°C and with equimolar concentration of the reactants. The runs carried out with variable concentration of the reactants in the reaction mixture at a temperature of -78°C with radiation intensity 30.6 rads/ min are listed in Table XVI. The temperature of the reaction was studied between -78°C and -25°C at a radiation intensity of 30.6 rads/min and with equimolar concentration of the reactants. The results obtained are tabulated in Table XVII. It may be noted that on several occasions the amount of the products recovered was negligible. This was attributed to impurities such as oxygen. Some of these results are shown in Table XV. However, they were not used for the kinetic study.

The correlation of the data using Equation(18), was made with a value of $\lambda = 9.0$(moles/liter) at -78°C. This value of λ corresponds to an equilibrium conversion of four moles/liter (i.e. $X_A=4.0$) of hydrogen sulfide at equimolar reactant concentration. The values of reaction rate constants thus obtained were averaged for any set of data obtained for variation of any particular parameter such as radiation intensity, composition, etc. In the following sections the values of the average rate constants are tabulated as functions of various parameters studied. In the time-composition diagrams shown in these sections, the solid curves are drawn using the average rate constants in Equation (18).

(a) Effect of Radiation Intensity

The experimental data obtained to study the effect of radiation intensity are listed in Tables XIII and XIV and are plotted in Figure 9. The values of the reaction rate constants used for the solid curves drawn using Equation (18),are tabulated in Table II. In Figure 9, it may be observed that only at the lowest intensity used, the experimental data show a slight inhibition period. The distribution of the products RSH and RSR as a function of hydrogen sulfide reacted is shown in Figure 10.

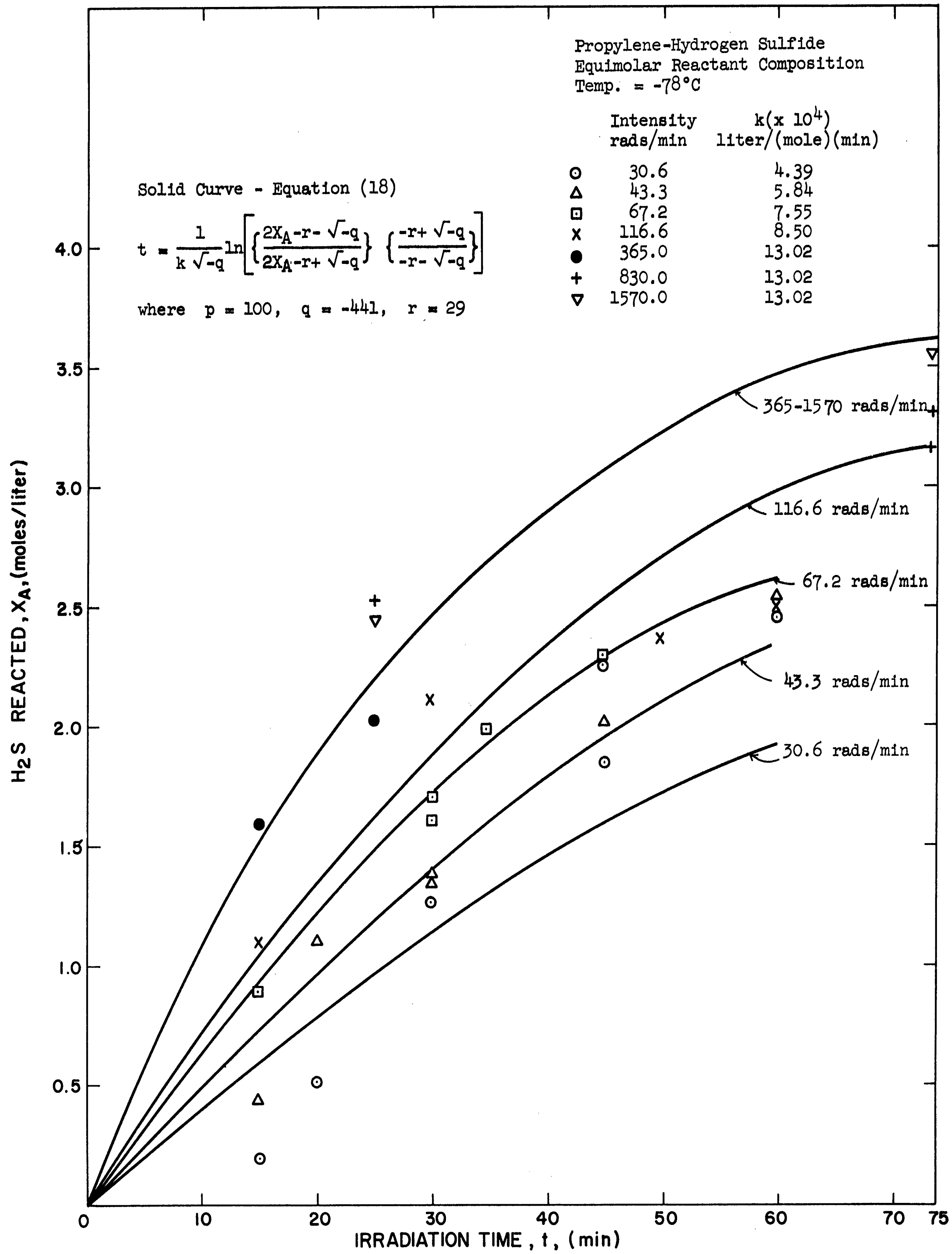


Figure 9. Conversion as a Function of Time for Propylene-Hydrogen Sulfide Reaction at Various Radiation Intensities.

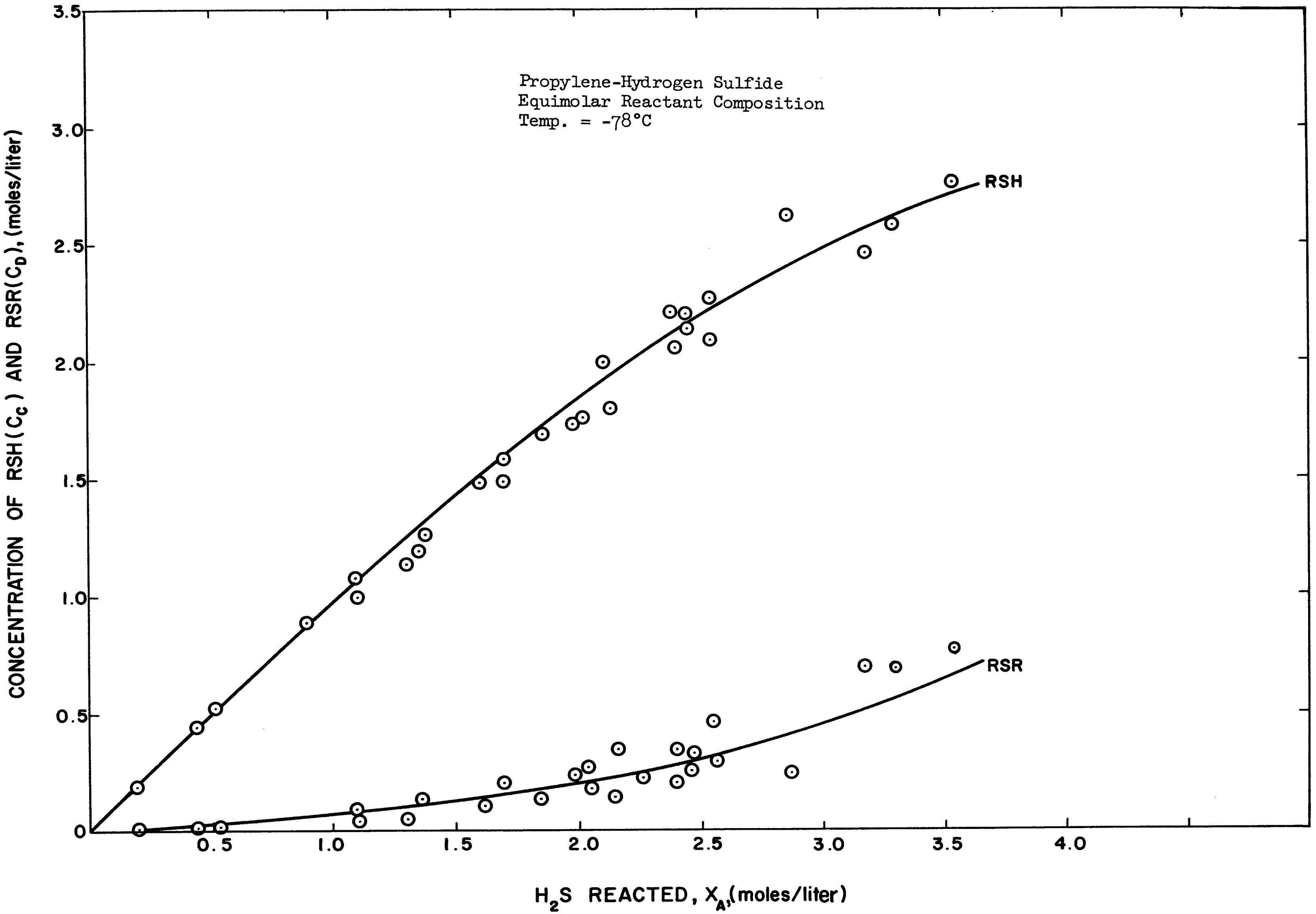


Figure 10. Propylene-Hydrogen Sulfide; Concentration of Propyl Mercaptan (RSH) and Propyl Sulfide (RSR) as a Function of Hydrogen Sulfide Reacted.

TABLE II

PROPYLENE-HYDROGEN SULFIDE: REACTION RATE CONSTANTS AT VARIOUS INTENSITIES

(Equimolar Reactant Composition; Temp. - -78°C)

Intensity rads/min	Reaction Rate Constant, $k(x10^4)$ liter/(mole)(min)
30.6	4.39
43.3	5.84
67.2	7.55
116.6	8.50
365-1570	13.02

The logarithm of the reaction rate constant k is plotted versus the logarithm of the radiation intensity in Figure 11. The solid line is drawn with a slope of 0.5, assuming an intensity function of $I^{0.5}$, which seems to be apparent for low intensities (30.6 to 116.6 rads/min). This line represents the average intensity function at low intensities and may be given in equation form as,

$$k = k' I^{0.5} = 8.5 \times 10^{-5} I^{0.5} \text{ liter/(mole)(min)} \qquad \ldots (20)$$

where k' is a redefined rate constant as indicated in Equation (20).

At higher intensities (365-1570 rads/min), however, the rate of the reaction does not seem to obey the square root dependence of the intensity of radiation and gradually becomes independent of the intensity. This phenomenon is discussed in the next chapter.

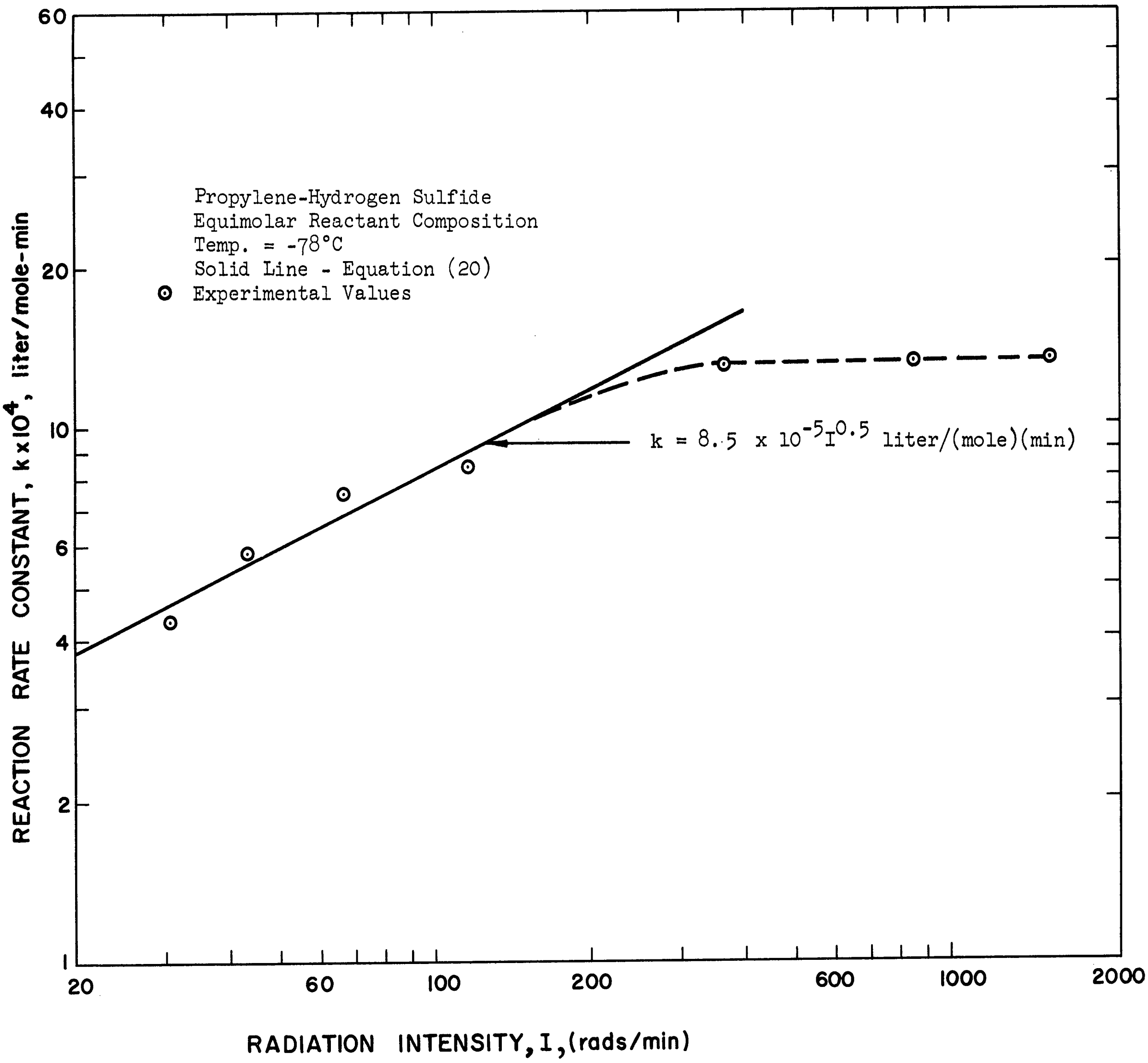


Figure 11. Effect of Radiation Intensity on the Propylene-Hydrogen Sulfide Reaction Rate Constant.

The experimental data for low intensity radiation were normalized to $I = 30.6$ rads/min assuming the intensity function of $I^{0.5}$. The reaction time t for any conversion X_A at an intensity I may be multiplied by a factor of $(I/30.6)^{0.5}$ to yield an equivalent reaction time for the same conversion at an intensity of 30.6 rads/min. This is true since, for any conversion with intensity as the only variable, the reaction time t is a function of the value of k as given by Equation (20). The normalized data are tabulated in Table XVIII and are plotted in Figure 12. The average value of the rate constant k, as obtained from this data is $(4.7 \pm 0.9) \times 10^{-4}$ liter/(mole)(min). However, if the fifteen minute data points at intensities of 30.6 and 43.3 rads/min are discarded assuming low yields due to inhibition effect, the data yields the value of k equal to $(5.0 \pm 0.7) \times 10^{-4}$ liter/(mole)(min). The latter value is used in Equation (18) to plot the solid curve in Figure 12.

The effect of the radiation intensity on the reaction rates was also obtained from average reaction rates for low intensity data and for conversions between ten and twenty-five per cent of the initial charge of H_2S. In order to use this approach the reverse reaction is neglected since C_A and C_B are greater than C_C. Equation (12) may then be rewritten as

$$R_{avg} = \frac{\Delta X_A}{\Delta t} = k_{avg} C_{Aavg} C_{Bavg} \qquad \ldots (21)$$

where the subscript 'avg' denotes an average value over any interval (i.e. R_{avg} = average rate).

Separating the intensity term, as done in Equation (20) but without assuming the intensity exponent as 0.5,

$$R_{avg}/C_{Aavg} C_{Bavg} = k_{avg} = k'_{avg} I^n \qquad \ldots (22)$$

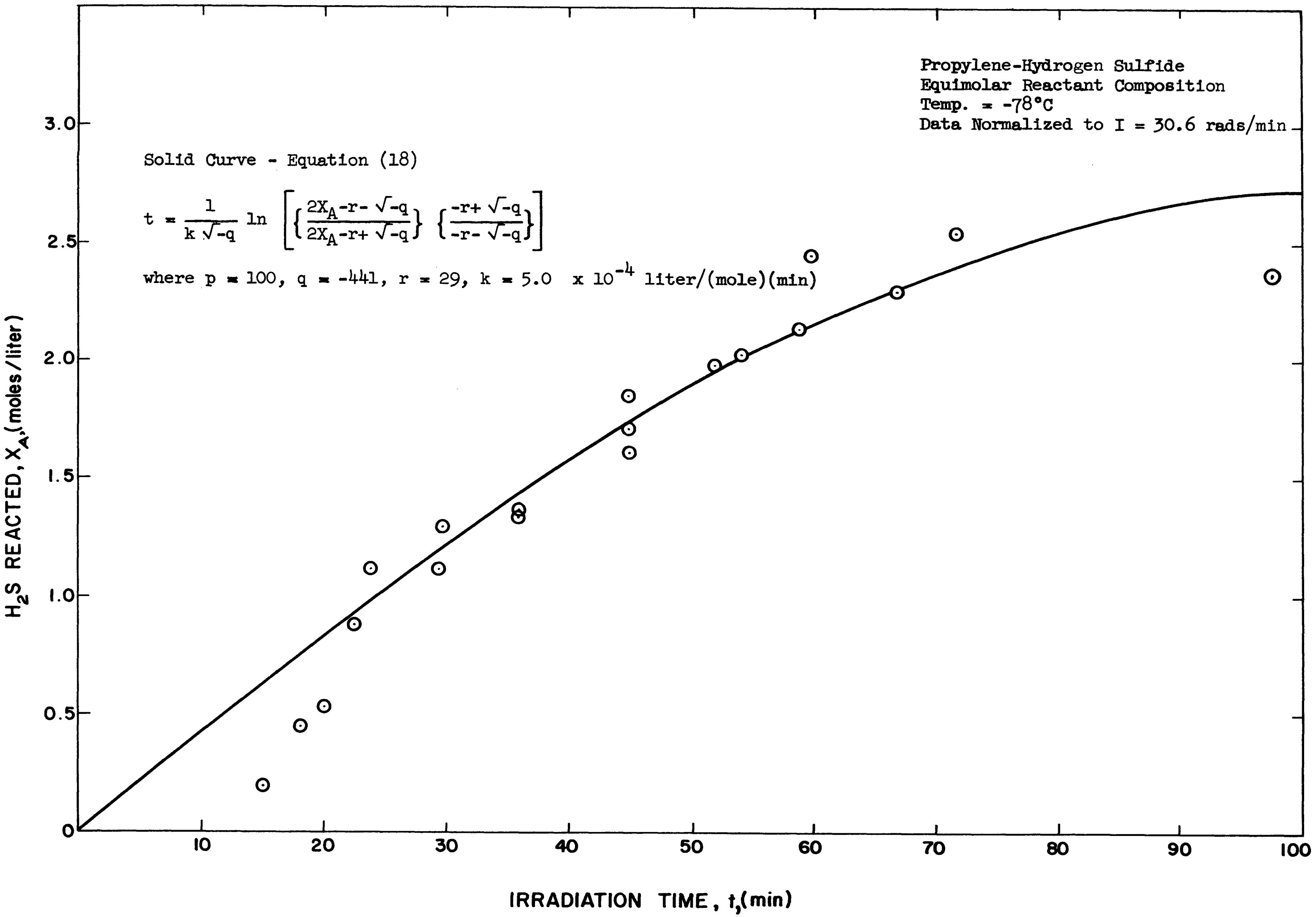


Figure 12. Conversion vs Time for Propylene-Hydrogen Sulfide Reaction; Low Intensity Data Normalized to I = 30.6 rads/min.

Equation (22) may be rewritten in logarithmic form as

$$\log(R_{avg}/C_{Aavg}C_{Bavg}) = \log k'_{avg} + n\log I \qquad \ldots (23)$$

The calculated values from experimental data to utilize Equation (23) are listed in Table XIX. These values are plotted in Figure 13(a). The method of averages as applied to these points yields the following relationship;

$$k_{avg} = 10.23 \times 10^{-5} I^{0.39} \text{ liter/(mole)(min)} \qquad \ldots (24)$$

Alternately if the intensity exponent is assumed to be 0.5, the data yield the value of k' equal to 8.23 x 10^{-5} liter/(mole)(min) which compares favorably with the previously obtained value (Equation(20). Utilizing this value of k' and combining Equations (21) and (22), one may also write the following equation for initial average rates and conversions,

$$X_A/C_{Aavg}C_{Bavg} = 8.23 \times 10^{-5} I^{0.5} t \qquad \ldots (25)$$

since $\Delta X_A = X_A - 0 = 0$ and similarly $\Delta t = t$.

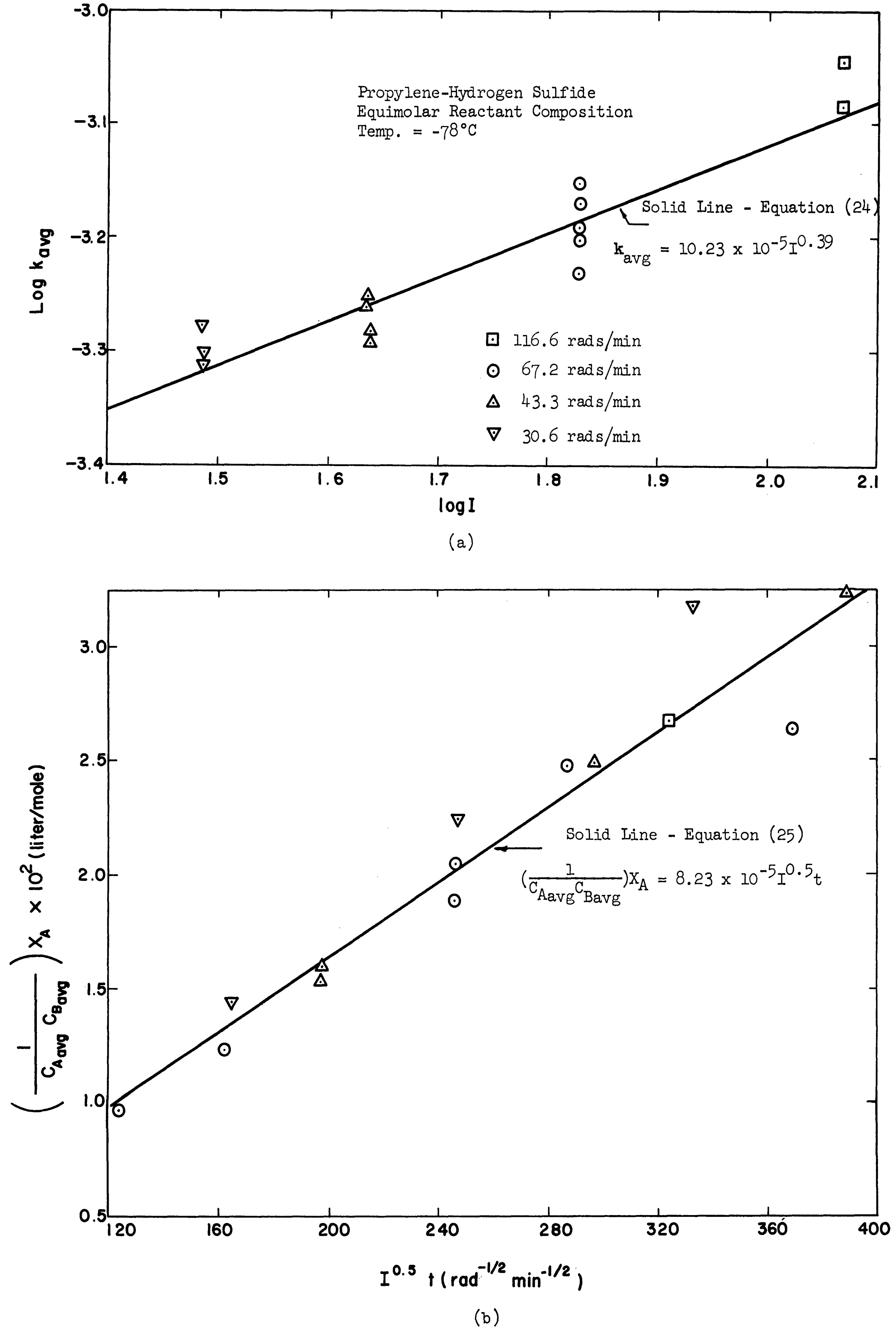
The values of $X_{Aavg}/C_{Aavg}C_{Bavg}$ as a function of $I^{0.5}t$ are tabulated in Table XIX and are plotted in Figure 13(b).

Some information regarding the secondary reactions resulting in the formation of propyl sulfide may be obtained since simultaneous concentrations of the products formed as a function of time and conversion of hydrogen sulfide are available. The rate equation for the formation of propyl sulfide may be written as,

$$\frac{d\left[C_3H_7SC_3H_7\right]}{dt} \simeq k_s \left[C_3H_6\right] \left[C_3H_7SH\right] \qquad \ldots (26)$$

or $$dC_D/dt = k_s C_B C_C \qquad \ldots (27)$$

where k_s is the reaction rate constant for the secondary reaction represented



(a)

(b)

Figure 13. Effect of Radiation Intensity on the Propylene-Hydrogen Sulfide Reaction.

by Equation (10). It may be noted that in Equations (26) and (27) the reverse reaction (i.e. decomposition of propyl sulfide) as shown in Equation (10), is neglected because of the low concentration of propyl sulfide.

Equation (27) may be combined with Equation (12) to eliminate the time variable. Neglecting the reverse reaction (Equation (12), for low conversions of H_2S), the combination of these equations yield

$$\frac{dC_D}{dX_A} = \frac{k_s C_B C_C}{k C_A C_B} = \left(\frac{k_s}{k}\right)\left(\frac{C_C}{C_A}\right) \qquad \ldots (28)$$

Equation (28), may be written for conversions in small increments as functions of average concentrations as

$$\frac{\Delta C_D}{\Delta X_A} = \frac{k_s}{k}\left(\frac{C_{Cavg}}{C_{Aavg}}\right) \qquad \ldots (29)$$

The calculations for k_s/k using Equation (29) and average concentrations obtained from Figure 10, for conversion of hydrogen sulfide between 1.0 and 2.5 moles/liter are listed in Table XX. The average value of k_s/k as obtained from these results is 0.96.

(b) Effect of Composition of Reaction Mixture

The amounts of the reactants in the reaction mixture were varied between four fold excess of hydrogen sulfide to four fold excess of propylene. During these investigations the temperature of the reaction was maintained at -78°C and the intensity of radiation used was 30.6 rads/min.

The results are tabulated in Table XVI (Appendix), and the time-composition curves are shown in Figure 14. In this figure the solid curves are drawn using Equation (18), and averaging the theoretical reaction times for concentration ratios of 2 and 0.5 and for concentration ratios of 4.0 and 0.25.

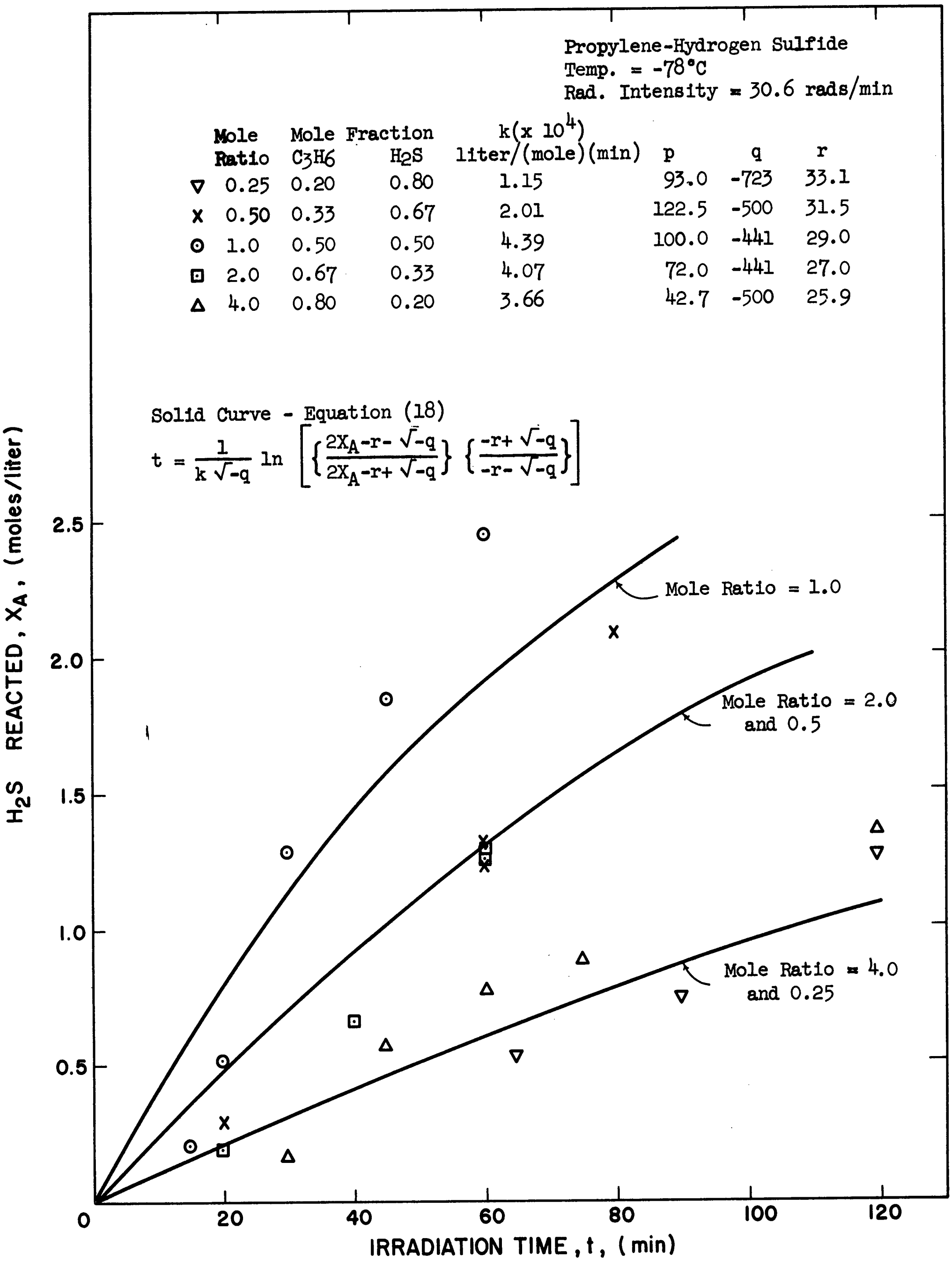


Figure 14. Conversion as a Function of Time for Propylene-Hydrogen Sulfide Reaction for Various Compositions of Reaction Mixture.

The product distribution is shown in Figure 15. The rate of the reaction as a function of the mole fractions of the components propylene and hydrogen sulfide are shown in Table III and Figure 16.

TABLE III

PROPYLENE-HYDROGEN SULFIDE
COMPOSITION EFFECTS ON REACTION RATE

(Temp. = -78°C; Rad. Int. = 30.6 rads/min)

Mole Ratio C_3H_6/H_2S	Mole Fraction C_3H_6	H_2S	Initial Reaction Rate moles/(liter)(min)	Rate Constant k(x10^4) liter/(mole)(min)
4.0	.80	.20	.0156	3.66
2.0	.67	.33	.0293	4.07
1.0	.50	.50	.0439	4.39
.50	.33	.67	.0246	2.01
.25	.20	.80	.0110	1.15

The rate of the reaction was highest for equimolar concentration of the reactants and decreased with an excess of either the addend, hydrogen sulfide, or the hydrocarbon, propylene. This is explained on the basis of the rate expressions derived in the following chapter. The distribution of the products of the reaction shows an effect that may be expected on the basis of the stoichiometry of the reactions (Equations (9) and (10)). The calculations for k_s/k using (Equation (29)) are listed in Table XX.

(c) Effect of Temperature

The temperature of the reaction was varied between -78°C and -25°C. The reaction mixture consisted of equimolar reactant concentration and the

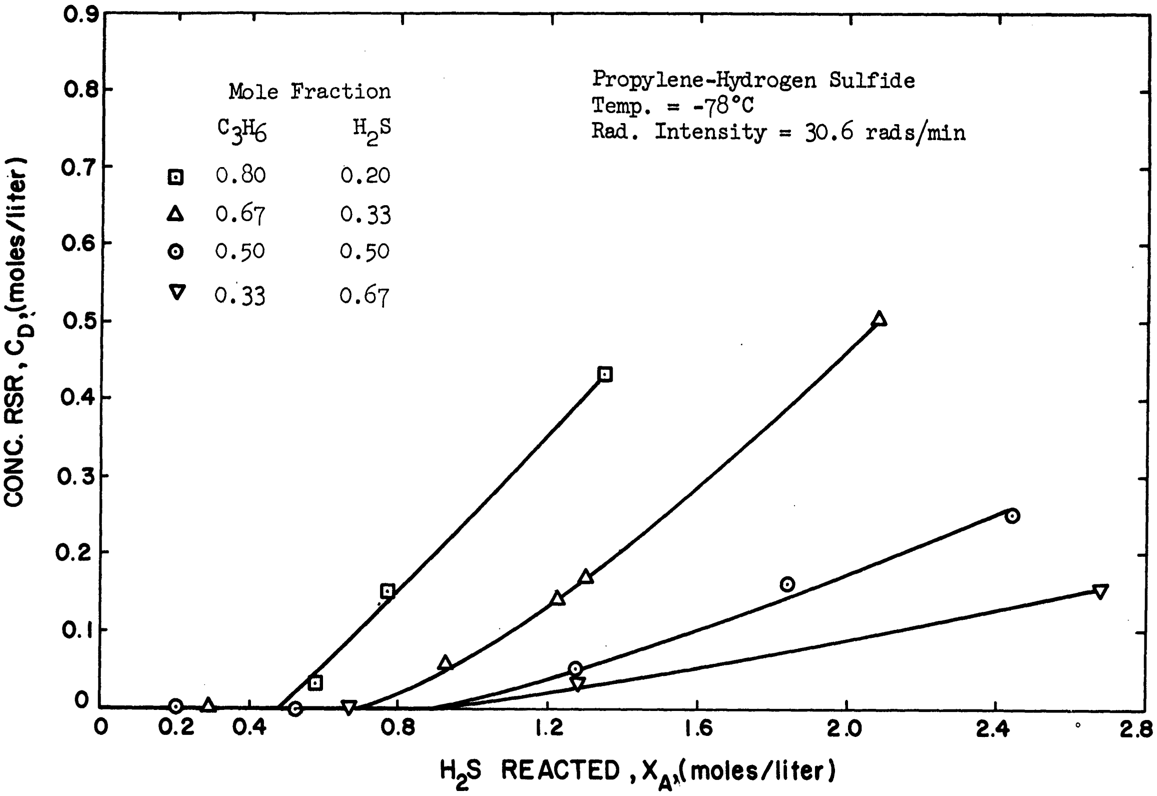


Figure 15. Effect of Composition on the Formation of Propyl Sulfide (RSR) for Propylene-Hydrogen Sulfide Reaction.

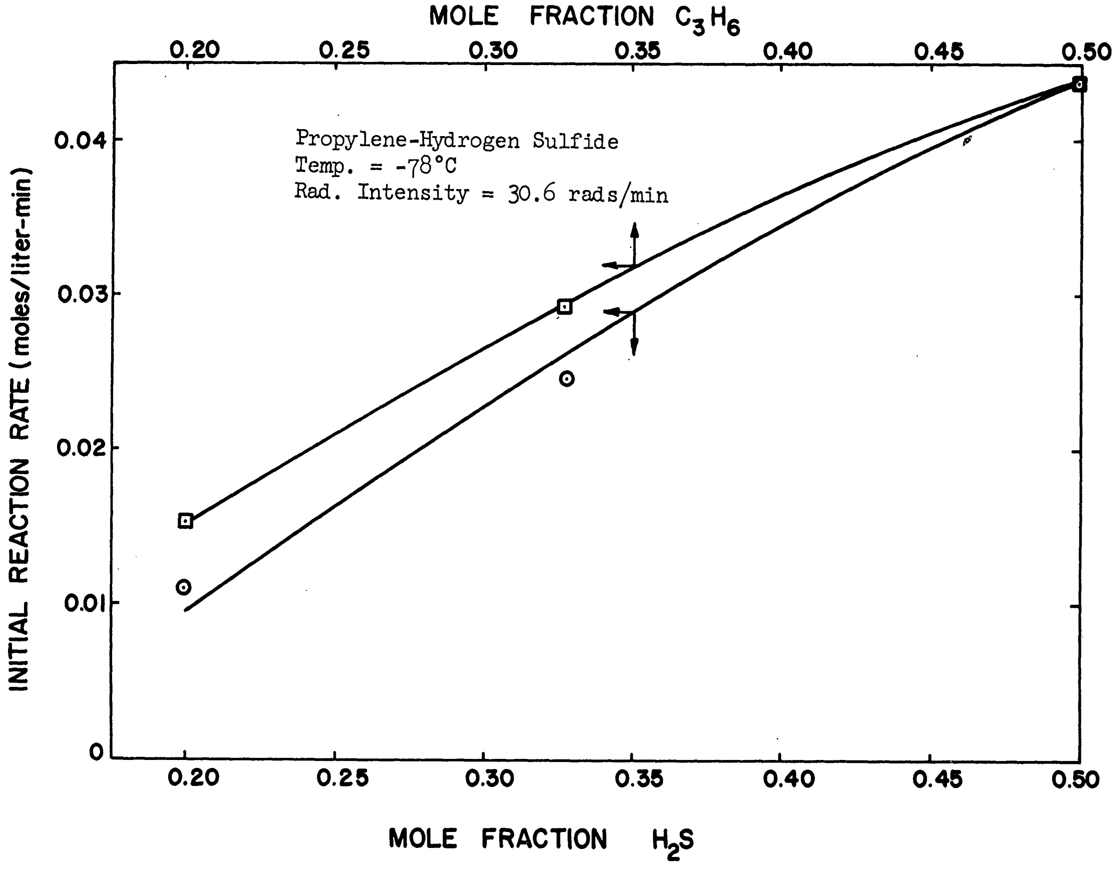


Figure 16. Effect of Composition on the Propylene-Hydrogen Sulfide Reaction Rate.

radiation intensity used was 30.6 rads/min. The results are tabulated in Table XVII (Appendix) and are plotted in Figure 17. In this figure the solid curve A is plotted using (Equation (18)) and a value of $\lambda = 9.0$ as mentioned before. For curve B, a value of λ equal to 16.3 is used. This value corresponds to an equilibrium conversion of three moles/liter (i.e. $X_A = 3.0$) of hydrogen sulfide. Duffey(26) reported lower equilibrium conversions of hydrogen sulfide at higher temperature. This is discussed in Chapter VI. Also, since the temperature effect is analyzed on the basis of initial rate, the value of does not have any effect on the analysis.

The results show that the variation of temperature between -78°C and -65°C had only a minor effect on the rate of the reaction. Unlike the reactors for radiations at temperatures of -78°C and -65°C, the reactors used for radiations at -25°C were thick-walled glass vials which were flame-sealed before irradiations. Considerable difficulties were encountered in the use of these vials, since hydrogen sulfide has a vapor pressure of approximately 5 atmospheres at -25°C. Several vials were broken after loading of the reactants and during the warm-up to this temperature. It is also believed that during the flame-sealing operation, the vacuum in the reaction tubes may not have been retained.

The results obtained show that at -25°C the conversion of hydrogen sulfide showed considerable scatter and some values were lower than at -78°C.

C. Reactions of Hydrogen Sulfide with Other Hydrocarbons

The addition reactions of hydrogen sulfide with three other hydrocarbons, butene-1, butene-2 and isobutene, were studied under the influence of gamma radiation. In all the cases equimolar quantities of the reactants were irradiated at a temperature of -78°C and with a radiation intensity between 1330 and 1570 rads/min.

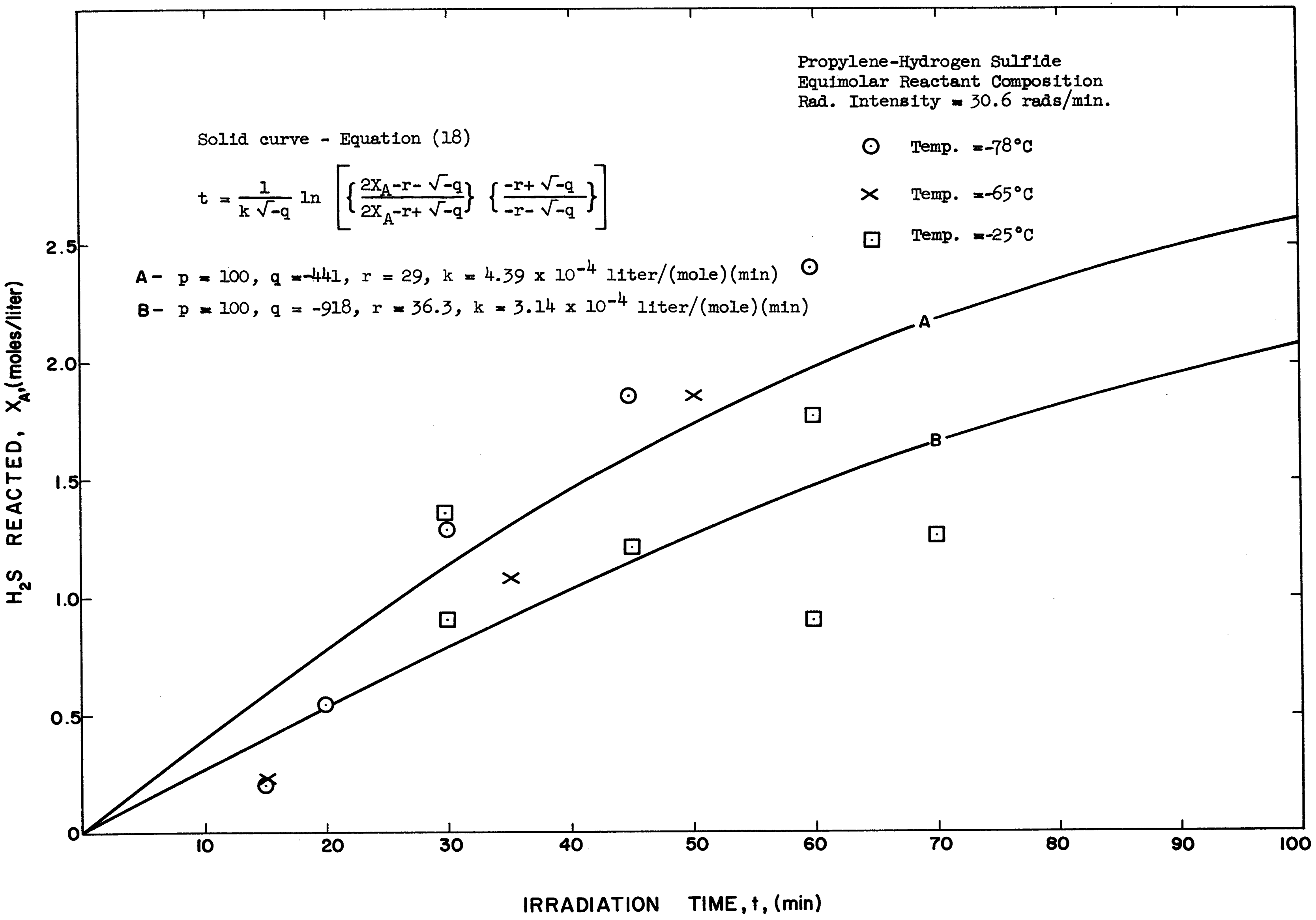


Figure 17. Conversion as a Function of Time for Propylene-Hydrogen Sulfide Reaction at Various Temperatures.

The chromatographic analysis showed the major products to be n-butyl mercaptan and n-butyl sulfide for butene-1, and isobutyl mercaptan and isobutyl sulfide for isobutene. The analysis of the products obtained for butene-2 showed a major chromatographic peak at a retention time slightly less than that for isobutyl mercaptan. Since the chromatographic peaks obtained for various mercaptans in this study were observed to follow the same order for retention times as for boiling points, this compound was identified as secondary butyl mercaptan. The boiling points of the secondary and isobutyl mercaptans are 85°C and 88.7°C respectively.

The per cent conversion and the G-values were considerably higher for butene-2 and isobutene, as compared to butene-1. However, yields for all the butenes studied were lower than those obtained for propylene. The results are reported in Table XXI (Appendix) and Figure 18. The solid curves in Figure 18 are drawn using a value of λ equal to 5.8 in Equation (18) which corresponds to an equilibrium conversion of 4.0 moles/liter of hydrogen sulfide. It may be noted that the notations C_B, C_C and C_D in Equation (18), are used to represent the hydrocarbon and corresponding mercaptan and sulfide (i.e. for butene-1, C_B, C_C and C_D represent the concentrations of butene-1, n-butyl mercaptan and n-butyl sulfide). The calculated radiation yields based on initial composition of the reaction mixture and the rate of disappearance of hydrogen sulfide are tabulated in Table IV. Comparable G-value for propylene is 9.7×10^4 at an intensity of radiation = 1570 rads/min. At lower radiation intensity G-values for propylene are much higher, owing to a more efficient use of radiation energy (Table XIV).

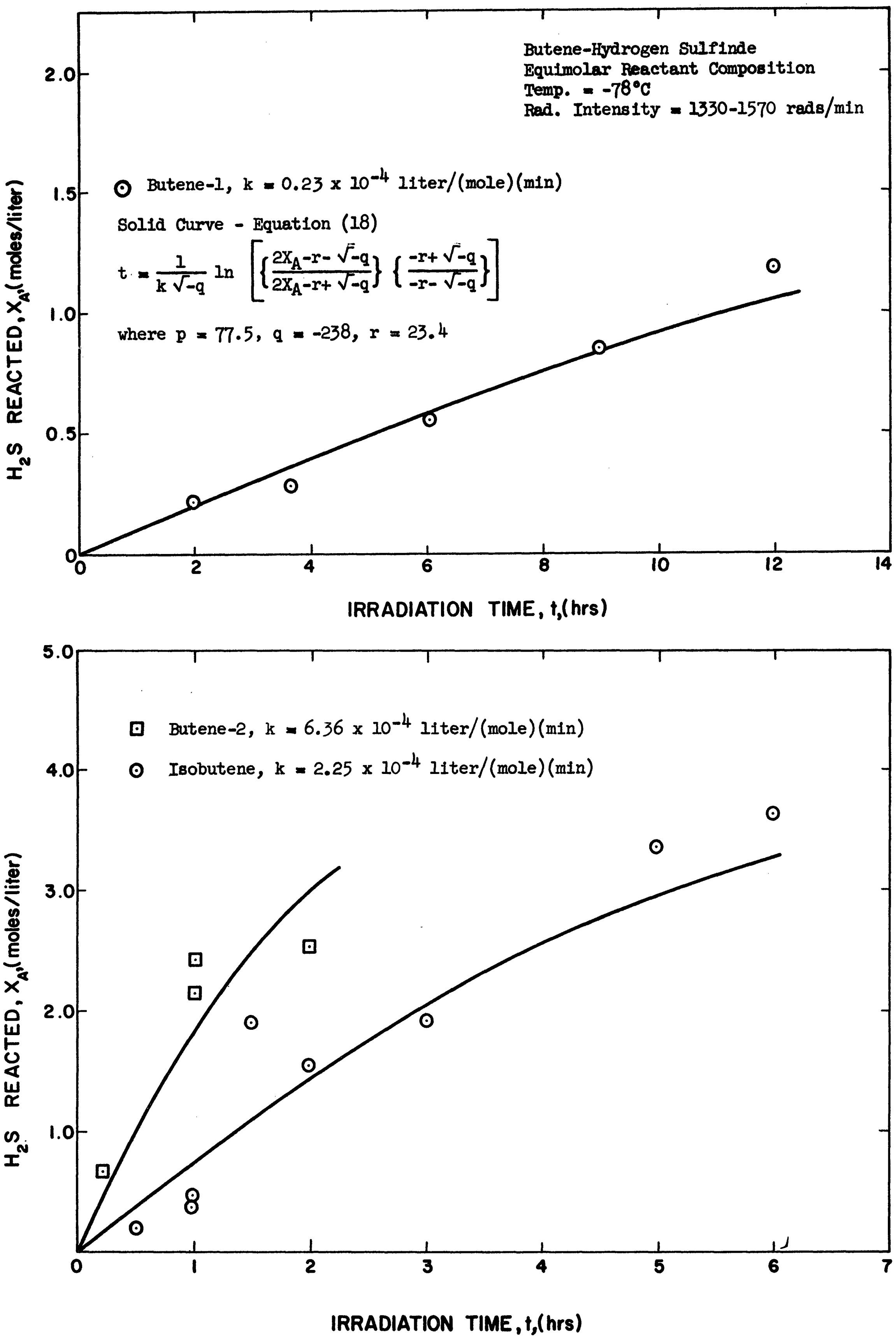


Figure 18. Conversion as a Function of Time for Butene-Hydrogen Sulfide Reaction: (a) Butene-1, (b) Butene-2, (c) Isobutene.

TABLE IV

BUTENE-HYDROGEN SULFIDE: RADIATION YIELDS AND REACTION RATE CONSTANTS

(Equimolar Reactant Comp.; Temp. = -78°C, Rad. Int. = 1330-1570 rads/min)

Hydrocarbon	G-Value ($-H_2S$)	Reaction Rate Constant $k(\times 10^4)$ liter/(mole)(min)
Butene-1	1.27×10^3	0.23
Butene-2	3.38×10^4	6.36
Isobutene	1.18×10^4	2.25

VI. ANALYSIS AND DISCUSSION OF THE RESULTS

In the preceding chapter, the experimental results are presented together with correlations based on the net reactions represented by Equations (9) and (10). However, it was also noted that the reaction seemed to occur by a free radical chain mechanism. In this chapter, the experimental evidence for the nature of the reaction is examined and compared with related studies in literature and a mechanism for the addition reaction is postulated. The mechanism is also supported by the structures of the products obtained. The postulation of the mechanism is followed by derivations of kinetic expressions. In the final section of this chapter the reactivities of the hydrocarbons studied in this investigation, and the effects of the radiation intensity, composition and temperature on the initial reaction rate for the propylene-hydrogen sulfide reaction, are discussed in view of the postulated mechanism, and derived kinetic expressions. Also, comparisons are made with the earlier correlations.

A. General Discussion

The addition reactions of hydrogen sulfide to simple olefins can be initiated by high energy gamma radiation as shown in the present investigation. The high radiation yields (G-value $> 10^3$) obtained for the reaction between hydrogen sulfide and propylene, butene-1, butene-2 or isobutene indicates that the reaction proceeds by a chain mechanism. Similar observations have been reported in the literature for reactions between hydrogen sulfide or organic mercaptans with olefinic hydrocarbons in the presence of peroxides or ultraviolet radiation.

For the reaction between thioglycolic acid and isobutene, Kharasch(53) proposed a chain mechanism initiated by thiyl (RS·) radicals. The proposed mechanism was similar to the one proposed for the addition reaction of hydrogen bromide with olefins.(52) In both cases the addition was termed "abnormal", since it took place contrary to Markownikoff's rule.

Sivertz(8,73) and his group studied the reaction of n-butyl mercaptan with 1-pentene. The initiation of the reaction was carried out by a photolytic method using 2-2'-azo-bis-isobutyronitrile. Fontijn(29) carried out identical experiments with high energy x- and gamma radiation. A chain reaction initiated by RS· radicals was proposed in both the studies.

Vaughn(92) proposed the following mechanism for the phto-addition of hydrogen sulfide to olefinic bonds:

$$H_2S \xrightarrow{h\nu} H\cdot + HS\cdot$$

$$HS\cdot + H_2C = CHR \longrightarrow HSCH_2\dot{C}HR$$

$$HSCH_2\dot{C}HR + H_2S \longrightarrow HSCH_2CH_2R + HS\cdot$$

The addition reactions of hydrogen sulfide with 1-butene and propylene were carried out at -78°C in quartz tubes which were illuminated with full radiation of a quartz mercury arc. The products were identified as n-butyl mercaptan and n-butyl sulfide for butene-1 reaction and n-propyl mercaptan and n-propyl sulfide for propylene reaction.

The nature of the products obtained for the addition reaction of hydrogen sulfide to various olefins under the influence of high energy gamma radiation in the present investigation suggest that the reaction is similar to the photochemical reaction.

A chain mechanism is proposed for the reaction (Section B) and is used to derive kinetic expressions. The proposal that the reaction is initiated by radicals is further supported by other observations. These are: (1) The presence of oxygen inhibits the reaction and (2) the rate of the reaction was found to be proportional to the squareroot of the intensity of radiation at low intensities. Such observations have been reported for a number of free radical reactions.

The importance of ionic mechanisms have been emphasized in some recent investigations.(17) This is particularly true for the polymerization of isobutene under the effect of high energy radiation in the presence of some solid particles. In the present study such processes are not considered important because of the following reasons: (1) the ionic process would yield a product according to the "normal" addition reaction, (2) the polymerization for the hydrocarbons by other mechanisms was considered to be insignificant as compared to the addition process. This is justified on the basis that the polymerization of the olefins considered in this study could be accomplished only with great difficulty, if at all, with the use of radiation. Since the competitive addition reaction of hydrogen sulfide is extremely rapid, the relative importance of the polymerization reactions would be negligible.

B. Mechanism of the Reaction

The interaction of gamma radiation with matter leads to the production of excited molecules or ions which in turn may produce free radicals. A schematic representation of various reaction processes considered to have a possible effect on the addition reactions studied is given on Page 69. The structures of possible intermediates are given on Page 70.

The initiating radicals for the reaction may be generated by direct splitting of H_2S molecules into the radicals H· and HS· under the influence of radiation. In an alternate process radiation energy may be absorbed by other molecules and transferred to H_2S via excitation transfer or ion neutralization and energy transfer or by a radical attack resulting in the formation of an HS· radical(Equations (30-33)).

The important chain propagation reactions are those by the HS· radicals (Equations (34) and (35) which yield mercaptans (or thiols) as reaction products. The energetics of these reactions are such that both the steps of addition and displacement take place without much energy barrier.(95) In contrast to this the attack by H· or R· radicals on hydrocarbon molecules would require considerable energy for chain propagation (Equations (36) and (37)). and hence may not be expected to compete with the reactions of HS· radicals. However, such radicals (H· or R·) may attack molecules of hydrogen sulfide, giving rise to HS· radicals (Equation (33)).

The inital attack of an HS· radical may occur on either of the two carbon atoms forming the double bond in a hydrocarbon molecule, as is indicated in the schematic representation of the structures of the possible intermediates for propylene, butene-1, butene-2 and isobutene shown on Page 70. The nature of the intermediates and its influence on the addition reaction is discussed in a later section.

Several other possible reactions may be postulated which can complicate the simplified propagation scheme. The alkyl radical $R\dot{C}HCH_2SH$ generated by the reaction of HS· radical with olefin(Equation (34)) may react with several molecules of olefin before reacting with a molecule of H_2S (Equation (35)). The products thus formed are known as "telomers". The product analysis showed that this is not an important process in the present study. Similar conclusions were reported by Onyszchuck(73) for the reaction of n-butyl mercaptan with 1-pentene and by El-Abbady(27) for the reactions of silicon hydrides with simple olefins.

Since the reaction product RCH_2CH_2SH can give rise to RS· radicals under the influence of radiation, secondary reactions are possible and are described by (Equations (38-40)).

The chains thus begun can end by mutual termination of such radicals (Equations (41-43)) resulting into the formation of organic sulfides and disulfides.

1. Reaction Processes

Initiation

$$H_2S \rightsquigarrow H\cdot + HS\cdot \qquad \ldots (30)$$

$$H\cdot + H_2S \longrightarrow H_2 + HS\cdot \qquad \ldots (31)$$

$$RR' \rightsquigarrow R\cdot + R'\cdot \qquad \ldots (32)$$

$$(\text{such as } CH_3\text{-}CH = CH_2 \rightsquigarrow CH_3\text{-}CH\text{-}\dot{C}H + H\cdot) \qquad \ldots (33)$$

$$R\cdot + H_2S \longrightarrow RH + HS\cdot$$

Chain Propagation

$$HS\cdot + RCH = CH_2 \longrightarrow R\dot{C}HCH_2SH \qquad \ldots (34)$$

$$R\dot{C}HCH_2SH + H_2S \longrightarrow RCH_2CH_2SH + HS \qquad \ldots (35)$$

Other Reactions

$$H\cdot + RCH = CH_2 \longrightarrow R\dot{C}HCH_3 \qquad \ldots (36)$$

$$RCHCH_3 + H_2S \longrightarrow RCH_2CH_3 + HS\cdot \qquad \ldots (37)$$

Secondary Reactions

$$R'SH \rightsquigarrow R'S\cdot + H\cdot \qquad \ldots (38)$$

$$R'S\cdot + RCH = CH_2 \longrightarrow RCHCH_2SR' \qquad \ldots (39)$$

$$RCHCH_2SR' + H_2S \longrightarrow RCH_2CH_2SR' + HS\cdot \qquad \ldots (40)$$

Termination

$$R\cdot + R\cdot \longrightarrow RR \qquad \ldots (41)$$

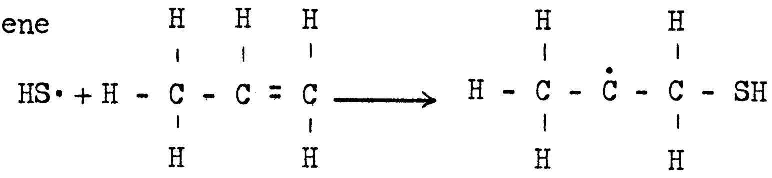
$$RS\cdot + R\cdot \longrightarrow RSR \qquad \ldots (42)$$

$$R'CH_2CH_2S + R'CH_2CH_2S\cdot \longrightarrow R''SR'' \qquad \ldots (43)$$

*R represents an organic radical (a prime is used to make arbitrary distinction between two such radicals).
A dot is used as a symbol to represent a free electron and is placed on an atom that represents an active center.

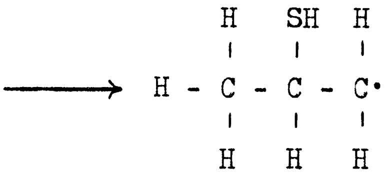
2. Structures of Some Possible Intermediates

a. Propylene



$$HS\cdot + H-\overset{H}{\underset{H}{C}}-\overset{H}{C}=\overset{H}{\underset{H}{C}} \longrightarrow H-\overset{H}{\underset{H}{C}}-\dot{C}-\overset{H}{\underset{H}{C}}-SH$$

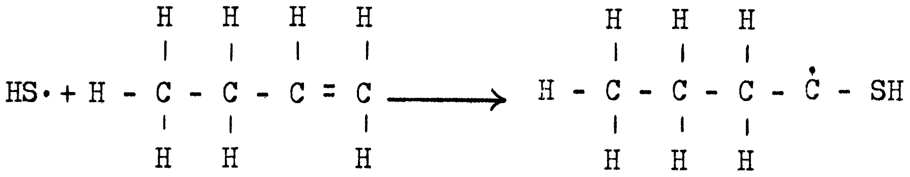
...(44)



$$\longrightarrow H-\overset{H}{\underset{H}{C}}-\overset{SH}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}\cdot$$

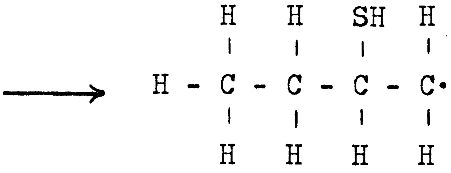
...(45)

b. Butene-1



$$HS\cdot + H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{C}=\overset{H}{\underset{H}{C}} \longrightarrow H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\dot{C}-SH$$

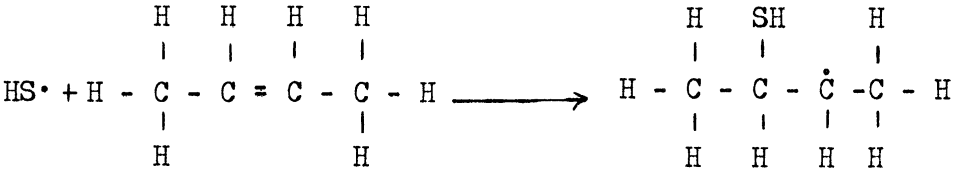
...(46)



$$\longrightarrow H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{SH}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}\cdot$$

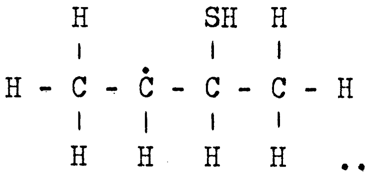
... (47)

c. Butene-2



$$HS\cdot + H-\overset{H}{\underset{H}{C}}-\overset{H}{C}=\overset{H}{C}-\overset{H}{\underset{H}{C}}-H \longrightarrow H-\overset{H}{\underset{H}{C}}-\overset{SH}{\underset{H}{C}}-\underset{H}{\dot{C}}-\overset{H}{\underset{H}{C}}-H$$

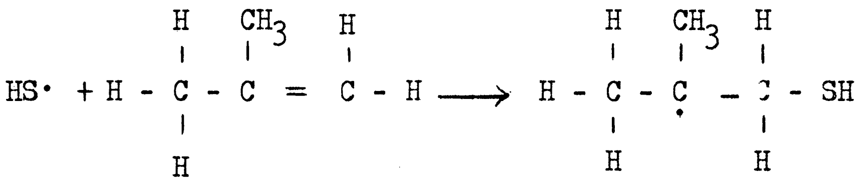
...(48)



$$H-\overset{H}{\underset{H}{C}}-\underset{H}{\dot{C}}-\overset{SH}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H$$

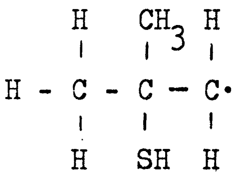
...(49)

d. Isobutene



$$HS\cdot + H-\overset{H}{\underset{H}{C}}-\overset{CH_3}{C}=\overset{H}{C}-H \longrightarrow H-\overset{H}{\underset{H}{C}}-\overset{CH_3}{\underset{\bullet}{C}}-\overset{H}{\underset{H}{C}}-SH$$

... (50)



$$H-\overset{H}{\underset{H}{C}}-\overset{CH_3}{\underset{SH}{C}}-\overset{H}{\underset{H}{C}}\cdot$$

... (51)

3. Derivation of Equations

In this section, a mechanism for the addition reaction of hydrogen sulfide to olefins is proposed in view of the discussion presented in the previous sections and considering only the significant reaction processes. The mechanism is utilized to derive kinetic equations. Even though the derivations are specifically referred to the propylene-hydrogen sulfide reaction, they may be considered applicable to the reactions of hydrogen sulfide with butene-1, butene-2 and isobutene. In derivation of the equations, the steady state approximation was assumed to be valid. The steady state approximation is based on the assumption that any reactive intermediate (such as free radical) in a chain reaction is present in a relatively small quantity and that the rate of formation of such an intermediate equals the rate of consumption. Thus the net rate of change of concentration of such an intermediate may be assumed to be zero. The assumption is valid after a brief initial period during which the radical concentration builds up to a steady state level.

The following equations and derivations describe the formation of the propyl mercaptan. The steady state approximation is assumed to be valid.

	Rate Constant	
(A) $H_2S \xrightarrow{h\nu} H\cdot + HS\cdot$	k_1	... (52)
(B) $H\cdot + H_2S \rightsquigarrow H_2 + HS\cdot$	k_2	... (53)
(C) $HS\cdot + C_3H_6 \longrightarrow \dot{C}_3H_7S$	k_3	... (54)
(D) $\dot{C}_3H_7S + H_2S \longrightarrow C_3H_7SH + HS\cdot$	k_4	... (55)
(E) $\dot{C}_3H_7S + \dot{C}_3H_7S \longrightarrow C_6H_{14}S_2$	k_5	... (56)
(F) $\dot{C}_3H_7S + HS\cdot \longrightarrow C_3H_8S_2$	k_6	... (57)
(G) $HS\cdot + HS\cdot \longrightarrow H_2S_2$	k_7	... (58)

The rate of the consumption of hydrogen sulfide may be written as,

$$-\frac{d[H_2S]}{dt} = \frac{d[C_3H_7SH]}{dt} = k_4 \, [H_2S] \, [\dot{C}_3H_7S] \qquad \ldots (59)$$

if the small amount of hydrogen sulfide consumed by the short chain Reaction Process B is ignored as compared to the large amount of hydrogen sulfide consumed by the Reaction Process D. It should also be noted that the rate of formation of propyl mercaptan is equated to the rate of consumption of hydrogen sulfide since it was demonstrated earlier that the propyl sulfide is formed from the initially formed propyl mercaptan.

The following equations describe the rate of change of concentration of various radicals:

$$\frac{d[H\cdot]}{dt} = 0 = k_1(I) - k_2 \, [H\cdot][H_2S] \qquad \ldots (60)$$

$$\begin{aligned} \frac{d[HS\cdot]}{dt} = 0 = {} & k_1(I) + k_2 [H\cdot][H_2S] - k_3 [HS\cdot][C_3H_6] \\ & + k_4[\dot{C}_3H_7S][H_2S] - k_6[\dot{C}_3H_7S][HS\cdot] \\ & - k_7[HS\cdot]^2 \end{aligned} \qquad \ldots (61)$$

$$\begin{aligned} \frac{d[C_3H_7S]}{dt} = 0 = {} & k_3[HS\cdot][C_3H_6] - k_4[\dot{C}_3H_7S][H_2S] \\ & - k_5[\dot{C}_3H_7S]^2 - k_6[HS\cdot][\dot{C}_3H_7S] \end{aligned} \qquad \ldots (62)$$

Equations (60), (61) and (62) are three simultaneous equations, two of which are quadratic. They can be solved to eliminate the concentration of the radicals. To facilitate the handling of the equations, the following substitutions are made:

$\left[\dot{C}_3H_7S\right] = X$

$\left[HS\cdot\right] = Y$

$\left[H\cdot\right] = Z$

$k_3\left[C_3H_6\right] = A$

$k_4\left[H_2S\right] = B$

$k_5 = C$

$k_7 = D$

$k_1\left(I\right) = F$

$k_2\left[H_2S\right] = G$

To simplify the solution of the equations, the termination constant k_6 may be expressed in terms of the termination constants k_5 and k_7 as follows:

$$k_6 = \varphi\sqrt{k_5k_7} = \varphi\sqrt{CD} = E \qquad \ldots(63)$$

where φ is a constant.

With these substitutions Equations (60-62) may be rewritten as follows:

$$F - GZ = 0 \qquad \ldots(64)$$

$$F + GZ - AY + BX - DY^2 - EXY = 0 \qquad \ldots(65)$$

$$AY - BX - CX^2 - EXY = 0 \qquad \ldots(66)$$

From Equation (64), $F = GZ$ ...(67)

Substituting this result in Equation (65):

$$2F - AY + BX - DY^2 - EXY = 0 \qquad \ldots(68)$$

Two new equations may be obtained by addition and subtraction of Equations (65) and (68):

$$2F = CX^2 + DY^2 + 2EXY \qquad \ldots(69)$$

$$2F = 2AY - 2BX - CX^2 + DY^2 \qquad \ldots(70)$$

Neglecting some insignificant and higher order terms, Equations (69) and (70) lead to the following solution:

$$Y = \frac{\sqrt{\{2F - X^2C(1-\varphi^2)\}} - \varphi\sqrt{CX}}{\sqrt{D}} \qquad \ldots(71)$$

$$X = \sqrt{\frac{2A^2F}{A^2C + 2AB\varphi\sqrt{CD} + B^2D}} \qquad \ldots(72)$$

Substituting for X and Y in Equation (59)

$$-\frac{d[H_2S]}{dt} = \frac{k_3k_4[C_3H_6][H_2S]\sqrt{2k_1(I)}}{\sqrt{\left\{k_3^2k_5[C_3H_6]^2 + 2k_3k_4\phi\sqrt{k_5k_7}[C_3H_6][H_2S] + k_4^2k_7[H_2S]^2\right\}}} \quad \ldots (73)$$

Equation (73) is somewhat complex. However, in the later part of this chapter, it is shown that this equation may be reduced to a simpler form, comparable to Equation (12) (Page 44).

If the intensity of radiation used is very high, one more derivation is needed for the case when the concentration of radicals is so high that the termination can take place by interactions of primary radicals, thus competing with the propagation reaction. In this case C and F would be competitive (Page 71).

The following two equations describe the rate of change of concentration of radicals, together with the steady state approximation:

$$\frac{d[HS\cdot]}{dt} = 0 = 2k_1(I) - k_3[HS\cdot][C_3H_6] + k_4[\dot{C}_3H_7S][H_2S] - k_6[HS\cdot][\dot{C}_3H_7S] \quad \ldots (74)$$

$$\frac{d[\dot{C}_3H_7S]}{dt} = 0 = k_3[HS\cdot][C_3H_6] - k_4[\dot{C}_3H_7S][H_2S] - k_6[HS\cdot][\dot{C}_3H_7S] \quad \ldots (75)$$

With the approximation that the concentration of the primary radicals $HS\cdot$, is much higher than the concentration of $C_3H_7S\cdot$, the following solution may be obtained,

$$-\frac{d[H_2S]}{dt} = \frac{k_3k_4}{k_6}[C_3H_6][H_2S] \quad \ldots (76)$$

This equation is independent of the radiation intensity.

The application of the equation derived in this section to the experimental data for propylene-hydrogen sulfide reaction is presented in the next section (Part 2), after a discussion on the reactivities of various hydrocarbons.

C. Effects of the Reaction Variables

1. Reactivities of Various Hydrocarbons

Amongst the four hydrocarbons studied propylene was found to be the most reactive with regards to the hydrogen sulfide addition reaction. The order of reactivities of the other hydrocarbons was butene-2 > isobutene > butene-1. This order agrees with the order of reactivities of these hydrocarbons with sulfur dioxide, reported by Bray.(15) This is explained below after the discussion of the course of the reaction.

The course of the reaction which can lead to the products observed for various hydrocarbons is shown by Equations (44), (46), (48) and (50) (Page 70). In all these cases the addition of the HS· radical is such that the intermediates formed are secondary or tertiary radicals. Equations (45), (47), (49) and (51) show an alternate course for the reactions, where the intermediates formed are primary radicals. Since it is known that the order of stability of radicals increases markedly along the series primary < secondary < tertiary, reactions are expected to follow the former course, i.e. as in Equations (44), (46), (48), and (50), agreeing with the experimental observations.

The high reactivity of propylene may be attributed to the stability of the secondary radical together with the energetics of the individual steps of the chain propagation. Reconsidering Reaction Processes (34) and (35) (Page 69)

$$HS\cdot + RCH=CH_2 \longrightarrow R\dot{C}HCH_2SH \qquad \ldots (34)$$

$$R\dot{C}HCH_2SH + H_2S \longrightarrow RCH_2CH_2SH + HS\cdot \qquad \ldots (35)$$

the first and the second reactions (Equations (34) and (35) respectively) are exothermic to the extent of 20 and 4 kcal/mole respectively at 25°C for the case of propylene-H_2S addition reaction. These values are obtained from the data on bond dissociation energies.(35) Sivertz(8) and his group concluded that for the case of isoprene and styrene (addition reaction with butyl mercaptan) reaction (35) is rate controlling while for the case of 1-pentene the rates of both the reactions (34 and 35) were high, though reaction (35) was somewhat slower, making the picture not so clear.

For butene-H_2S reaction, however, the exothermicity decreases by 4 kcal/mole for Reaction Process (34), if it is assumed that the methyl group decreases the dissociation energy by 4 kcal/mole.$^{(95)}$ The reaction rate, particularly for Reaction Process (35), may be considerably slower in that case. Thus the butene-H_2S reaction may be considerably slower than the propylene-H_2S reaction.

Since the isobutene radical is tertiary, it would be considerably more stable and this probably reduces the rate of the addition reaction. The higher reactivity of butene-2 as compared to butene-1 may be accounted for on the basis that butene-2 may produce two secondary radicals (Page 70) by the attack of HS· radical on either of the C atoms number 2 or 3, while butene-1 produces one primary and one secondary radical. The formation of n-butyl mercaptan as the major product shows that the primary radical is rather unreactive.

The G-values obtained for the reactions of these hydrocarbons with hydrogen sulfide were in the range of the G-values obtained for the n-butyl mercaptan-pentene-1 reaction by Fontijn.$^{(29)}$ Direct comparison with the work of Vaughn$^{(92)}$ on photoaddition of hydrogen sulfide to olefins could not be made since the conversions and the strength of the light source, etc. are not obtainable.

2. Propylene-Hydrogen Sulfide Reaction

The kinetic equations derived from the proposed mechanism are shown on Pages 71-74. In derivations of these equations the approximation of constant steady state concentration of radicals was made in all cases.

The complexity of the kinetic equations is partially due to the fact that the chain reaction may be terminated by a number of processes. This may be particularly true in the present investigation because of the high concentrations of the hydrocarbon and hydrogen sulfide present in the reaction mixture.

In this section the experimental data for the propylene-hydrogen sulfide reaction is disucssed with respect to the proposed mechanism and the derived equations. Comparisons with respect to the data reported in literature are made wherever feasible. The studies by Sivertz(8), Onyszchuck(73) and Fontijn(29) on the butyl mercaptan-1-pentene system are indirectly applicable. In his study of the olefin-H_2S reaction Vaughn(92) did not report any kinetic data and hence comparisons are not possible.

(a) Effect of Radiation Intensity.

Reconsidering Equation (73) (Page 74), it is observed that the rate of reaction is proportional to the squareroot of radiation intensity. This is based on the assumption that termination of the chain reaction occurs via interaction of two radicals. This assumption is justified since the reactions were studied in the liquid phase and hence wall termination may be expected to be negligible. Also the high rates of chain propagation reactions indicated by high G-values suggest that the production of inactive radicals, particularly on the alkyl type, would be negligible. The experimental data plotted in Figure 11 show that the intensity dependence of the reaction rate is predicted by the rate expression between approximately 30-150 rads/min. Such intensity dependence of reaction rate was also shown by Sivertz(8), Onyszchuck(73), and Fontijn(29) in their studies.

At high intensities of radiation Equation (73) may not be expected to predict the effect of intensity on the reaction rate, since the interactions of primary radicals may compete with the propagation steps as explained in the derivation of Equation (76) (Page 74). In such a case the efficiency of the use of radiation energy decreases. The experimental data plotted in Figure 11 indicate that as according to Equation (76) the rate becomes independent of the intensity of radiation above approximately 300 rads/min. The decrease of the intensity exponent from 0.5 to 0 has been encountered in several cases and has been reviewed by Chapiro.(18)

(b) Effect of Composition

The effect of the composition of the reaction mixture on the reaction rate and on the product distribution is shown in Table III and in Figures 14-16. From Table III it is observed that the reaction rate is highest at equimolar concentration of reactants and falls off as the concentration of one of the reactants increases and the concentration of the other decreases. In Figure 16 the reaction rate is plotted against the mole fraction of hydrogen sulfide and propylene in the reaction mixture. It should be noted here that the experimental conditions used imposed a limitation that the concentrations of the two reactants could not be varied independently, i.e., the effect of one of the reactants on the reaction rate could not be studied independently, keeping the concentration of the other reactant constant.

Rate Equation (73) indicates that the reaction rate is a complex function of concentrations of both the reactants. A further complicating feature is the value of φ which may affect the reaction rate, depending upon the concentrations of various radicals and their reactivities with one another. Onyszchuck(73) and Sivertz(8) have reported considerations of the value of φ in their studies on photochemical reactions of butyl mercaptyl and alkyl radicals. The complex concentration dependence of the reaction of butyl mercaptan and 1-pentene was also observed by Fontijn,(29) working with high energy radiation, even though no quantitative correlations were reported.

The product distribution (Figure 15) shows that at high olefin/H_2S ratio of concentrations, there is an increase in the concentration of propyl sulfide which is expected on the basis of the stoichiometry of the reactions.

i . Mathematical Treatment of Rate Equations

In this section the various rate equations derived, particularly the generalized Equation (73), are reformulated to analyze the experimental data obtained to study the effect of composition of the reaction mixture. The approach is divided into the following steps:

(ia) Examination of Equation (73) for maximum rate.

(ib) General treatment of the equation and validity of the assumptions.

(ic) Simplified treatment with the assumption that $\varphi = 1$.

(id) Overall kinetics and estimation of the rate constants.

(ia) Examination of Equation (73) for maximum rate.

Rate Equation (73), as derived, is as follows:

$$-\frac{d(H_2S)}{dt} = \frac{k_3k_4\left[C_3H_6\right]\left[H_2S\right]\sqrt{2k_1(I)}}{\sqrt{\left\{\begin{matrix} k_3^2k_5\left[C_3H_6\right]^2 + 2k_3k_4\varphi\sqrt{k_5k_7}\left[C_3H_6\right]\left[H_2S\right] \\ + k_4^2k_7\left[H_2S\right]^2 \end{matrix}\right\}}} \quad \ldots (73)$$

This equation may be handled with less difficulty if the concentration terms are expressed in terms of mole fractions of the reactants. The resulting new expression, in such a case, may be related to the above expression by using appropriate factors for the total charge of reactants and the volume of the reaction system.

With the following substitutions,

α = mole fraction H_2S

β = mole fraction C_3H_6

$R = \dfrac{\text{mole fraction, } H_2S \text{ Reacted}}{\text{min}}$

$A' = k_3k_4\sqrt{2k_1(I)}$

$B' = k_3^2k_5$

$C' = k_4^2k_7$

$$R = \frac{A'\alpha\beta}{\left\{B'\alpha^2 + 2\sqrt{B'C'} + C'\beta^2\right\}^{\frac{1}{2}}} \qquad \ldots (79)$$

one of the two variables α and β may be eliminated as follows,

Since

$$\alpha + \beta = 1, \qquad \beta = 1 - \alpha$$

Substituting for β in terms of α

$$R = \frac{A'\alpha(1-\alpha)}{\left\{B'\alpha^2 + 2\varphi\sqrt{B'C'}\,\alpha(1-\alpha) + C'(1-\alpha)^2\right\}^{\frac{1}{2}}} \qquad \ldots (80)$$

Equation (80) may be rewritten as,

$$R = \frac{A'\alpha(1-\alpha)}{\left\{\alpha^2(B'-2\varphi\sqrt{B'C'} + C') + \alpha(2\varphi\sqrt{B'C'}-2C') + C'\right\}^{\frac{1}{2}}} \qquad \ldots (81)$$

and regrouping the constants by using the following notations,

$$a_1 = B'-2\varphi\sqrt{B'C'} + C'; \qquad a_2 = 2\varphi\sqrt{B'C'} - 2C'$$

one may obtain,

$$R = \frac{A'\alpha(1-\alpha)}{(a_1\alpha^2 + a_2\alpha + C')^{\frac{1}{2}}} \qquad \ldots (82)$$

Since the experimental data show that the rate has a maximum value as a function of the mole fraction of any component, the derivative of R with respect to α may be equated to zero, to find the point at which this maximum occurs. Hence,

$$R' = \frac{dR}{d\alpha} = \frac{(a_1\alpha^2 + a_2\alpha + C')^{\frac{1}{2}}A(1-2\alpha) - A\alpha(1-\alpha)\frac{1}{2}(a_1\alpha^2 + a_2\alpha + C')^{-\frac{1}{2}} + (2a_1\alpha + a_2)}{a_1\alpha^2 + a_2\alpha + C'}$$

$$= 0 \qquad \ldots (83)$$

Equation 83 may be rearranged as,

$$R' = \frac{(a_1\alpha^2 + a_2\alpha + C')(1-2\alpha)A - A\alpha(1-\alpha)\frac{1}{2}(2a_1\alpha + a_2)}{(a_1\alpha^2 + a_2\alpha + C^1)^{3/2}} = 0 \qquad \ldots (84)$$

The following deduction can be made from Equation (84),

$$(a_1\alpha^2 + a_2\alpha + C')A(1-2\alpha) = A\alpha(1-\alpha)\frac{1}{2}(2a_1\alpha + a_2) \qquad \ldots (85)$$

The experimental value of the maximum rate was found at $\alpha = 0.5$. Thus from Equation (85),

$$2a_1\alpha + a_2 = 0 \qquad \ldots (86)$$

since α and $1-\alpha$ are not equal to zero,

$$\therefore \quad 2a_1\alpha = -a_2 \qquad \ldots (87)$$

or

$$a_1 = -a_2 \qquad \ldots (88)$$

If the maximum does not truly occur at $\alpha = 0.5$, one may deduce from Equation (85) that

$$2(a_1\alpha^2 + a_2\alpha + C')(1-2\alpha) = \alpha(1-\alpha)(2a_1\alpha + a_2) \qquad \ldots (89)$$

which may be rewritten as,

$$-2a_1\alpha^3 + a_2(\alpha - 3\alpha^2) - 4\alpha C' + 2C' = 0 \qquad \ldots (90)$$

Substituting for the values of a_1 and a_2, in Equation (88),

$$B' - 2\phi\sqrt{B'C'} + C' = 2C' - 2\phi\sqrt{B'C'} \qquad \ldots (91)$$

which indicates that $B' = C'$. This conclusion is independent of the value of φ. Expressed in terms of rate constants it indicates that,

$$k_3^2 k_5 = k_4^2 k_7 \qquad \ldots (92)$$

or

$$k_3/k_4 = \sqrt{k_7/k_5} \qquad \ldots (93)$$

(ib) <u>General Treatment of Rate Equation and Validity of the Assumptions</u>.

Rate Equation (80), which is a reformulation of the generalized Equation (73), may be simplified by using the conclusion derived in the preceding section that $B' = C'$. Thus Equation (80),

$$R = \frac{A' \alpha (1-\alpha)}{\left\{B' \alpha^2 + 2 \sqrt{B' C'}\, \varphi\, \alpha (1-\alpha) + C' (1-\alpha)^2\right\}^{\frac{1}{2}}} \qquad \ldots (80)$$

may be rewritten as,

$$R = \frac{A'}{\sqrt{B'}} \; \frac{\alpha (1-\alpha)}{\left\{\alpha^2 + 2 \varphi \alpha (1-\alpha) + (1-\alpha)^2\right\}^{\frac{1}{2}}} \qquad \ldots (94)$$

$$= k'' \; \frac{\alpha (1-\alpha)}{\left\{\alpha^2 + 2 \varphi \alpha (1-\alpha) + (1-\alpha)^2\right\}^{\frac{1}{2}}} \qquad \ldots (95)$$

where $k'' = A' / \sqrt{B'} = k_4 \sqrt{2k_1 (I) / k_5}$

In the derivation of this rate equation it was pointed out that the treatment of the kinetic equations may be simplified by designating φ as a factor that relates the termination rate constants of like and unlike radicals, and where φ was defined as

$$\varphi = k_6 \Big/ \sqrt{k_5 k_7} \qquad \ldots (63)$$

It should be noted here that k_5 and k_7 as defined in the present study represent interactions between two like radicals and are often designated as $2k'_5$ and $2k'_7$ in the literature. In that case, $k_6 = 2\phi\sqrt{k'_5 k'_7}$. However, in this situation one should introduce a statistical factor of $\frac{1}{2}$ in the value of ϕ , since at equal concentrations collisions between unlike species are twice as probable as those between either like species.

The value of ϕ for several reaction systems has been investigated and reported in literature.(10,84,95) Even though large values of ϕ are reported(96) for some systems, the geometric mean corresponding to $\phi = 1$ as defined above adequately represents systems where differences in polarity of the reactants or resonance stabilization are not important. For the free radical reaction between n-butyl mercaptan and 1-pentene, ϕ values between 0.5 and 1 have been reported.(73,84) It should be noted here that in several copolymerization systems, it has been reported that ϕ varies with monomer feed ratios.(95)

The constants k'' and ϕ in the rate Equation (95) may be evaluated by trial and error from the kinetic data. Defining a new constant μ by,

$$\phi = 1 + \mu \qquad \ldots (96)$$

where μ can be positive or negative, one may reformulate the rate Equation (95) as follows:

$$R = k'' \frac{\alpha(1-\alpha)}{\left\{\alpha^2 + (1+\mu)\alpha(1-\alpha) + (1-\alpha)^2\right\}^{\frac{1}{2}}} \qquad \ldots (97)$$

and since $\alpha + (1-\alpha) = 1$,

$$R = k'' \frac{\alpha(1-\alpha)}{\left\{1+2\mu\ \alpha(1-\alpha)\right\}^{\frac{1}{2}}} \qquad \ldots (98)$$

$$\therefore\ R = k''\ \alpha\ (1-\alpha)\left\{1+2\mu'\alpha(1-\alpha)\right\}^{-\frac{1}{2}} \qquad \ldots (99)$$

and if it is assumed that $2 > \mu > -2$, since the maximum value of $\alpha(1-\alpha) = 0.25$, Equation (99) may be expanded to give

$$R = k''\ \alpha\ (1-\alpha) + k''\ \mu\ \left\{\alpha(1-\alpha)\right\}^{2} \qquad \ldots (100)$$

neglecting higher order terms.

The trial and error correlation of the reaction rate with composition according to Equation (99) was attempted with positive, negative, and zero values for μ. The positive, negative, and zero values of μ have the following meanings: If μ is positive, ϕ is > 1 (Equation(96)) and hence the crosstermination between two unlike radicals is favored over the interaction between two like radicals. The zero value of μ indicates that $\phi = 1$, which corresponds to the geometric mean as already described. If $\mu = -1$, $\phi = 0$ and represents a limiting case whereby crosstermination is not favored and the termination occurs by mutual interaction between like radicals only. The calculations indicated that the best correlation was obtained with $\mu = 0$ (i.e. $\phi = 1$) which is represented by Curve A in Figure 19. In drawing this curve the rates are defined by a dimensionless parameter R/R_{max} where R_{max} is the rate at $\alpha = 0.5$. The data are listed in Table V.

TABLE V

PROPYLENE HYDROGEN SULFIDE:COMPOSITION EFFECTS ON INITIAL REACTION RATES

(Temp. = -78°C; Rad. Intensity = 30.6 rads/min)

Mole Fraction C_3H_6	 H_2S	Initial Reaction Rate (x10^3) Mole Fr., H_2S Reacted/min	R/R_{max}
0.80	0.20	0.95	0.43
0.67	0.33	1.61	0.73
0.50	0.50	2.20	1.0
0.33	0.67	1.09	0.49
0.20	0.80	0.45	0.204

It may be observed in Figure 19, that curve A does not fit the experimental data for unequal concentrations of propylene and hydrogen sulfide (i.e. when $\alpha \neq 0.5$). Such a deviation from the generalized rate equation maybe explained on the basis that the propagation steps may be hindered by other reaction processes, particularly that of energy transfer, which would result in a decrease in the efficiency of utilization of radiation energy, which will further result in a lower rate of the reaction. It is also possible that the value of φ may vary with concentration ratio of the reactants. In such a case φ should be determined by separate determination of rate constants k_5, k_6 and k_7 by isolating the various radicals and studying them with methods such as the rotating sector method. In this method the reaction mixture is subjected to intermittent illumination (or radiation) by introducing a rotating plate (from which a sector has been cut out) between the reaction mixture and the source of light. The kinetic data obtained by

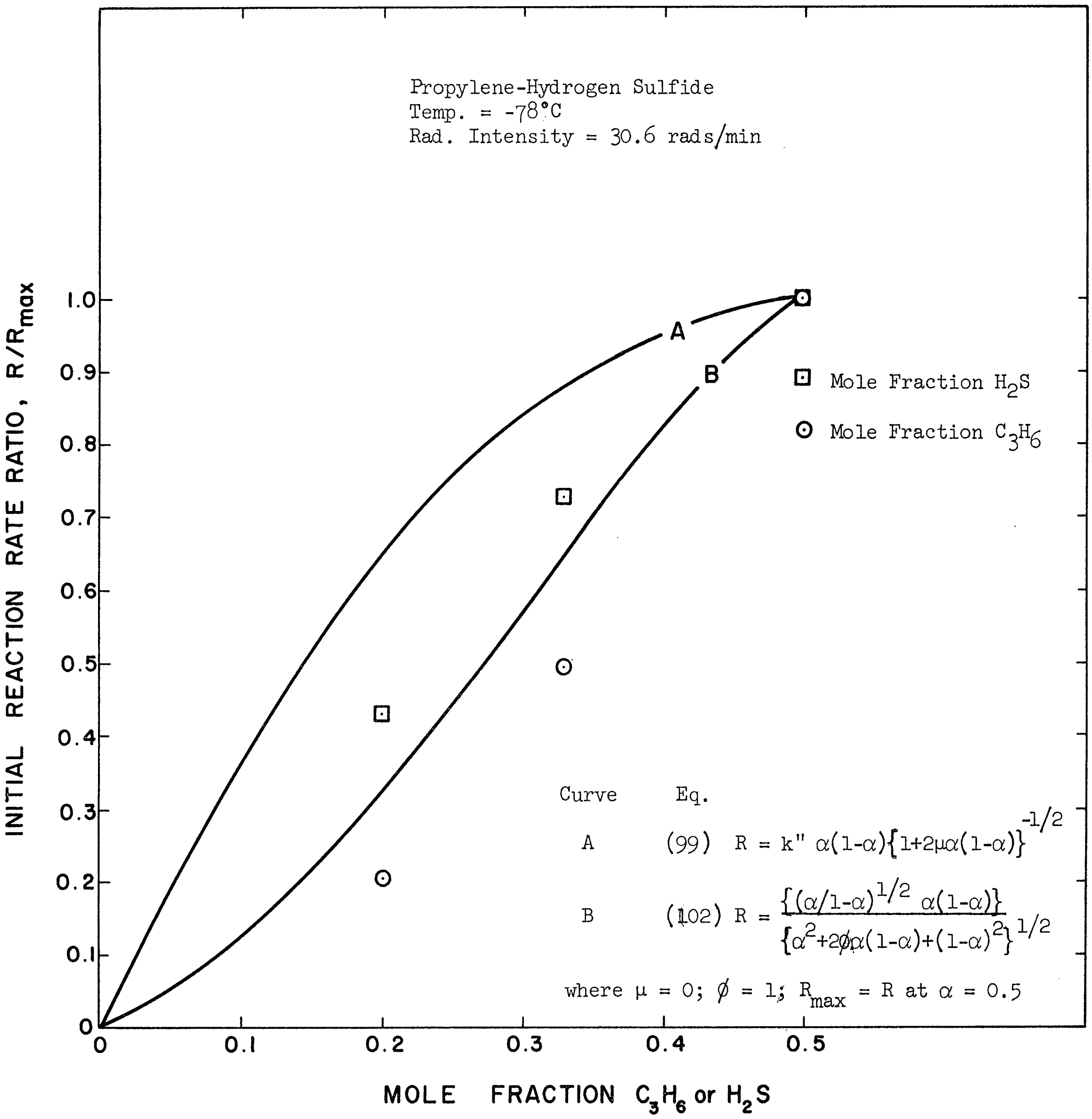


Figure 19. Propylene-Hydrogen Sulfide; Ratio of Reaction Rate and Maximum Rate as a Function of Mole Fraction of the Reactants in the Reaction Mixture.

this unsteady state method may be combined with those obtained by the steady state method to yield separate values for termination and propagation rate constants.(96)

The correlation of the reaction rates with the composition taking into account the energy transfer processes is attempted in the following section. Such energy transfer processes are reported by Nevitt(72) for the radiolysis of mixtures of butyl mercaptan, octene-1 and benzene. He observed that a sensitization effect was produced by octene-1 which increased the free radical yield, while the reaction was deactivated by the presence of benzene. Such phenomena can not be explained by what is termed as the "simple dilution effect".(18) For radiation polymerization of vinyl monomers in the presence of a solvent, the "simple dilution effect" proposes that the free radical yield is a linear function of the monomer content of the reaction mixture. Chapiro(18) has suggested correlations of such energy transfer processes whereby reaction rate is presented as a function of the mole fractions of the monomer and the solvent through their effects on the initiation rate.

In the derivation of the rate Equation (73), the initiation rate was taken as $\sqrt{2k_1(I)}$ to represent the intensity function. At compositions other than the equimolar concentration of the reactants, this initiation rate may be modified by a factor of f, relating it to the mole fractions of the components in the reaction mixture α and β (or $1-\alpha$). In modification of these rate equations only the fractional values of $\alpha/1-\alpha$ are used since it is determined that the reaction rate assumes a maximum value at equimolar reactant concentration. Thus

$$R_i = \left\{2k_1If\right\}^{\frac{1}{2}} = \left\{2k_1(I)(\alpha/1-\alpha)\right\}^{\frac{1}{2}} \qquad \ldots (101)$$

and the rate Equation (73) as represented by Equation (95) (with notations as on Page 79) may be modified as follows:

$$R = k'' \frac{\{(\alpha/1-\alpha)^{\frac{1}{2}}\ \alpha(1-\alpha)\}}{\{\alpha^2 + 2\,\phi\,\alpha(1-\alpha) + (1-\alpha)^2\}^{\frac{1}{2}}} \qquad \ldots (102)$$

A plot of R/R_{max} as a function of α according to Equation (102) together with the experimental values obtained is shown in Figure 19 (Curve B). It may be noted from Figure 19, that transfer reactions seem to be more important at high concentration of hydrogen sulfide.

(ic) Simplified Treatment of Rate Equation

The generalized rate Equation (73) may be simplified if it is assumed that ϕ =1. Such an assumption would represent a valid approximation, since in the rate Equation (95) (reformulated Equation (73)),

$$R = \frac{k''\alpha(1-\alpha)}{\{\alpha^2 + 2\,\phi\,\alpha(1-\alpha) + (1-\alpha)^2\}^{\frac{1}{2}}} \qquad \ldots (95)$$

a small deviation in the value of ϕ would have a minor effect on the reaction rate. With ϕ =1, Equation (95) may be rewritten as,

$$R = k''\alpha(1-\alpha) \qquad \ldots (103)$$

Equation (103) represents a reduced form of the generalized rate Equation (73) which was derived from the postulated mechanism for the addition reaction. This equation is essentially similar to Equation (12) which was derived to express the reaction rate as a function of concentrations of the reacting species involved in the net reactions only and according to the stoichiometry of the reactions.

(id) Overall Kinetics and Estimation of the Individual Rate Constants

In the preceding sections, the experimental results are analyzed to obtain overall reaction rates. The results of such overall kinetics do not provide the values of the individual rate constants k_1-k_7 for initiation, propagation and termination steps in the postulated mechanism. However, they may be estimated from the results of this study and some other results reported in literature, as follows.

The value of the initial reaction rate at equimolar concentration of the reactants at -78°C and radiation intensity equal to 30.6 rads/min is 0.044 moles/(liter)(min), (Page 58). Substituting the value of the initial concentrations of reactants equal to 10 moles/liter in Equation (103), (in concentration terms) and recalling the definition of k" (Page 82).

$$k'' = k_4 \sqrt{2k_1(I)/k_5} = 4.4 \times 10^{-4} \text{ liter/(mole)(min)} \qquad \ldots (104)$$

In order to estimate the values of k_1 and k_5 the following assumption and calculations are made. It is assumed that the reactivities of radicals is independent of the size of the molecules as is done in polymerization reactions. In that case the termination constants may be assumed to be equal to those obtained by Onyszchuck$^{(73)}$ for n-butyl mercaptan and 1-pentene reaction. Thus

$$k_5 = 3 \times 10^{11} \text{ liter/(mole)(min)}; \quad k_7 = 3 \times 10^{12} \text{ liter/(mole)(min)}$$

The estimation of the initiation rate constant, k_1, may be made as follows. Assuming a G-value of 3 for the radical production the following calculations may be made.$^{(20,7)}$ Since 3 molecules converted is equivalent to 100 ev of energy absorbed, one mole would require energy equivalent to,

$$1 \text{ mole} \Bumpeq \frac{100}{3} \frac{\text{ev}}{\text{molecules}} \times 6.02 \times 10^{23} \frac{\text{molecules}}{\text{mole}} \times 1.6 \times 10^{-12} \frac{\text{ergs}}{\text{ev}}$$

$$\Bumpeq 3.21 \times 10^{13} \text{ ergs}$$

$$\therefore \quad 1 \frac{\text{mole}}{\text{gm}} \Bumpeq 3.21 \times 10^{13} \text{ ergs/gm}$$

Since 5.70 gms of the reaction solution occupies 7.5cc, dividing by density

$\rho = 5.70/7.5$ gms/cc

$$1 \frac{\text{mole}}{\text{liter}} \Bumpeq 3.21 \times 10^{13} \text{ ergs/gm} \times \frac{1 \text{ rads}}{100 \text{ ergs/gm}} \times \frac{1}{1000 \times 5.70/7.50} \frac{\text{gms}}{\text{liter}}$$

$$\Bumpeq 3.3 \times 10^{8} \text{ rads}$$

and hence the rate constant for initiation is,

$$k_1 = \frac{1 \text{ mole/liter}}{3.3 \times 10^{8} \text{ rad}} = 3 \times 10^{-9} \text{ moles/(liter)(rad)} \qquad \ldots (105)$$

Substituting values of k_1 and k_5 in Equation (104),

$$k_4 = 4.4 \times 10^{-4} \times \sqrt{\left(3 \times 10^{11}\right)/2 \times (3\times10^{-9})I}$$

and since I = 30.6 rads/min

$$k_4 = 5.6 \times 10^{5} \text{ liter/(mole)(min)} \qquad \ldots (106)$$

Also by using Equation (92),

$$k_3 = k_4 \sqrt{k_7/k_5} \qquad \ldots (92)$$

$$= 5.6 \times 10^{5}\sqrt{10}$$

$$= 1.8 \times 10^{6} \text{ liter/(mole)(min)} \qquad \ldots (107)$$

Since by definition, $k_6 = \sqrt{k_5 k_7}$, (assuming $\varphi = 1$)

$$k_6 = \sqrt{3 \times 10^{11} \times 3 \times 10^{12}}$$

$$= 9.5 \times 10^{11} \text{ liter/(mole)(min)} \qquad \ldots (108)$$

(c) Effect of Temperature

The experimental data obtained to study the effect of temperature on the reaction between hydrogen sulfide and propylene are plotted in Figure 17. It may be observed that the reaction rate was little affected between the temperatures of -78°C and -65°C and the data are correlated by using the value of the average reaction rate constant k equal to 4.39×10^{-9} liter/(mole)(min) The lack of the effect of temperature between -78°C and -65°C may be explained on the basis that the thermal contributions to the generation of free radicals is neglegible and that the individual steps of propagation and termination in the reaction mechanism have low activation energies.

Even though the results at -25°C show considerable scatter, the yields were lower, in general, than those at -78°C. A decrease in the reaction yield with increase in temperature for the case of the propylene-hydrogen sulfide reaction was reported by Duffey.(26) Sivertz(84) found negative overall activation energies for reactions of methyl mercaptan with isobutylene, propylene and ethylene in the gas phase and attributed it to reversibility of the addition reaction of thiyl radical to the olefin,

$$RS\cdot + CH = CHR' \rightleftharpoons RSCH_2\dot{C}HR' \qquad \ldots. (109)$$

If the rate of the reaction is actually lower, then it is indicated that the change in the equilibrium constant for an equivalent reaction

$$HS\cdot + CH_3CH = CH_2 \rightleftharpoons CH_3\text{-}\dot{C}H\text{-}CH_2SH \qquad \ldots (110)$$

for the present study adversely affects the reaction yield with an increase in temperature. This may be expected since the decomposition reaction of the radical C_3H_7S may be expected (the reverse reaction yielding HS· and C_3H_6

Equation (110)) to compete favorably with the displacement reaction (Equation (111)).

$$CH_3\text{-}\dot{C}H\text{-}CH_2SH + H_2S \longrightarrow CH_3\text{-}CH_2\text{-}CH_2SH + \cdot SH \qquad \ldots (111)$$

It should be noted, however, that the experiments at -25°C were conducted at a pressure of approximately five atmospheres as compared to subatmospheric pressures for experiments at -78°C, which may or may not have any effect.

An estimate of the activation energy for the addition reaction may be made as follows. The Arrhenius equation for the reaction rate constant as a function of temperature may be written as,

$$k = Ae^{-\Delta H_A/RT} \qquad \ldots (112)$$

where k = Reaction rate constant (at any temperature T)

ΔH_A = Activation energy for the reaction

A = Frequency factor

T = Temperature (°K) and R = 1.987 cal/(mole)(°K)

For the reaction rate constants at -78°C (195°K) and -25°C(248°K) Equation (112) may be rewritten as,

$$\ln \frac{k_{195}}{k_{248}} \quad - \frac{\Delta H_A}{1.987}\left(\frac{1}{195} - \frac{1}{248}\right) \qquad \ldots (113)$$

Since the experiments at -78°C and -25°C were conducted at similar reactant composition (equimolar) and radiation intensity (30.6 rads/min), the ratio of average initial rates may be considered to be equivalent to the ratio of the reaction rate constants. From the experimental data and Figure 19, the initial reaction rates at -78°C and -25°C, are obtained as 0.044 and 0.031 moles/(liter)(min) respectively, yielding the ratio of the reation rates at -78°C and -25°C equal to 1.42 .

Hence,

$$k_{195}/k_{248} = 0.044/0.031$$

$$= 1.42 \qquad \ldots (114)$$

Substituting in Equation (113),

$$-\Delta H_A = 1.987 \ln 1.42/(1/195 - 1/248)$$

$$= -650 \text{ cal/mole} \qquad \ldots (115)$$

It should be noted that this value refers to the overall apparent activation energy only.

(d) Secondary Reaction.

In chapter VI, it was noted that the propyl mercaptan formed by the reaction of hydrogen sulfide with propylene may react further with propylene to form propyl sulfide. The ratio k_s/k for the reaction rate constant for the propylene-propyl mercaptan reaction (k_s) and for the propylene-hydrogen sulfide reaction (k) was found to be 0.96 from the analysis of the data obtained for the reaction conducted with equimolar concentrations of propylene and hydrogen sulfide at -78°C. This result merely indicates that the reactivities of propyl mercaptan and hydrogen sulfide for addition to the olefinic double bond are approximately equal. It also indicates an equivalent mechanism for the two reactions.

The data obtained for the propylene-hydrogen sulfide reaction with varying composition were also analyzed to obtain the k_s/k ratio (Table XX). The results indicate that, with propylene concentration higher than the concentration of hydrogen sulfide in the reaction mixutre, the ratio of k_s/k is generally greater than one, and for the reverse case, k_s/k is less than one. This effect may be caused by the difference in transfer reactivities of various radicals occurring in the system.

VII. SUMMARY AND CONCLUSIONS

The addition reactions of hydrogen sulfide to propylene, butene-1, butene-2 and isobutene can be successfully initiated by cobalt-60 gamma radiation, in the liquid phase and in the absence of oxygen. Under identical conditions, the reaction did not seem to occur without the use of radiation.

The addition reactions were rapid and gave high radiation yields. The G-values obtained were greater than 10^3. The reactivities of the olefins followed the order, propylene $>$ butene-2 $>$ isobutene $>$ butene-1. The high G-values indicate that the addition reaction occurs by a chain mechanism. The postulated mechanism suggests that the chains are initiated by HS· radicals generated from the decomposition of hydrogen sulfide under the effect of radiation. The proposed free radical mechanism is supported by the analysis of the nature of the products obtained and by the observed inhibiting influence of oxygen on the reaction.

The major products of the reaction between hydrogen sulfide and propylene were normal propyl mercaptan and normal propyl sulfide. The nature of the products indicate that the addition is "abnormal," i.e., contrary to the Markownikoff's rule. Similar results have been reported for the photochemical addition of hydrogen sulfide to olefinic hydrocarbons.(92)

The investigation of the propylene-hydrogen sulfide reaction kinetics indicated that at low intensities (between approximately 30 - 150 rads/min) the reaction rate was proportional to the squareroot of radiation intensity. This phenomena supports the postulated free radical mechanism. The low-intensity rate data obtained at a temperature of -78°C and with equimolar reactant concentration, were fitted by the expression

$$R = 8.5 \times 10^{-5} I^{0.5} \left[C_3H_6\right]\left[H_2S\right] \text{ moles/(liter)(min)}$$

where R is defined by the rate of disappearance of hydrogen sulfide. At higher intensities, however, the intensity exponent seemed to decrease, and the reaction rate was found to become independent of the radiation intensity above approximately 350 rads/min.

Since no solvent was used, the concentrations of the reactants were varied relatively to study their effects on the initial rates for the propylene-hydrogen sulfide reaction. The effect of composition on the reaction is discussed in view of the rate equations derived from the proposed reaction mechanism.

Temperature variation between -65°C and -78°C, when the reaction was carried out at subatmospheric pressures, did not seem to effect the rate of the propylene-hydrogen sulfide reaction. Some experiments were carried out at -25°C at superatmospheric pressures in heavy-walled glass reactors. It was found that the rate of the reaction was lower than that at -78°C. Since the formation of thiyl radicals is known to be reversible, the effect is attributed to an adverse effect of temperature on the equilibrium constant for the reaction involving the formation and decomposition of the intermediate.

VIII. SUGGESTIONS FOR FURTHER WORK

The addition of hydrogen sulfide to some olefinic double bonds under the effect of gamma radiation is accomplished with comparative ease at low temperature, as opposed to high temperatures required for conventional catalytic methods. An added advantage is that the reaction proceeds in a specific direction under the influence of radiation, eliminating a complex mixture of isomers. This should find both direct and indirect applications in similar organic synthesis.

The photoaddition of hydrogen sulfide to vinyl chloride (resulting in ethylene thiochlorohydrin), 2-chlorobutene-2, allyl alcohol, etc. have been reported in literature.(92) It is suggested that the studies on the effect of gamma radiation on these and similar reactions may result into some useful information. An effort could also be made to synthesize some commercially important mercaptans and other sulfur compounds using high energy radiation.

On the theoretical side, further studies on the addition reactions of hydrogen sulfide with unsaturated organic compounds, may be directed towards deriving more information on the structures and reactivities of these compounds. One important aspect, not studied in the present work, is the effect of substituents on the reactivities of olefins and other unsaturated compounds.

The present study was conducted with batch reactors. A study with continuous reactors and flow methods could add greatly to the knowledge about the kinetics of the reactions. Such a study may be particularly useful with regards to the information about secondary reactions. Some recent advances in techniques, such as pulse radiolysis, may be used to study the rates of individual steps in the chain reaction.

IX. APPENDIX

A. Physical Properties

TABLE VI

PHYSICAL PROPERTIES OF PERTINENT COMPOUNDS*

Compound	Mol. Wt.	Density**	M. P. °C	B. P. °C
Propylene	42.08	$.6095^{-47}$ $.65^{-78}$	-185	-47
Hydrogen sulfide	34.08	$.96^{-60}$ $.99^{-78}$	-82.9	-61.8
1-Butene	56.10	$.71^{-78}$	-130	-5
2-Butene, Cis(22.3%)	56.10	$.73^{-78}$	-139	(Cis)1
Trans(77.2%)	56.10	$.73^{-78}$	-106	(Trans)2.5
Isobutene	56.10	$.71^{-78}$	-140.7	-6
n-Propyl mercaptan	76.15	.8357	-111.5	68
Isopropyl mercaptan	76.15	.8055	-130.7	60
n-Propyl sulfide	118.23	$.814^{17}$	-101.9	141-2
Isopropyl sulfide	118.23	$.810^{25}$		120.4
Propyl disulfide	150.29	.814	-102	192
n-Butyl mercaptan	90.18	.8365	-115.9	98
Isobutyl mercaptan	90.18	.8357	-79	88
n-Butyl sulfide	146.29	.852	-79.7	182
Isobutyl sulfide	146.29	.8386		172
Toluene	92.13	.867	-95	110.6

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*The data were obtained from the following references: (1) The International Critical Tables, (2) Lange's Handbook of Chemistry.

**All densities are at 25°C unless specified otherwise.

B, Dosimetry

TABLE VII

CORRECTION FACTORS AND DOSE FACTORS FOR DOSIMETRY

Temperature of Measurement °C	Correction Factor	Dose Factor
20	1.0014	28.7
21	1.007	28.5
22	1.00	28.3
23	.993	28.1
24	.986	27.9
25	.979	27.7
26	.972	27.5
27	.966	27.3

TABLE VIII

DECAY-CORRECTION FACTORS FOR COBALT-60

Time Interval (months of decay)	Correction Factor (I/I_0)
0	1.0
3	0.9674
6	0.9360
9	0.9056
12	0.8762
15	0.8476
17	0.8292

TABLE IX

DOSIMETRY DATA

Date	Sample* Position cms	Irr. Time mins	O. D.**	Temp. °C	Dose Rate rads/min
4/1/61	CW	22	1.22	22	1570
	5	22	0.66	22	833
	28	22	0.283	22	366
	37.5	40	0.305	22	216
	49.5	40	0.175	22	124
	63	40	0.107	22	75.7
12/1/61	46	125	0.608	25.5	134
	66	125	0.304	25.5	67.2
	96	250	0.275	25.5	30.8
	96	540	0.570	23.5	29.6
	110	540	0.425	23.5	21.7
	96[a]	540	0.615	23.5	31.8
8/24/62	75	150	0.227	22	42.9
	94	150	0.142	22	27.0

*All distances indicated are from outside of cage. CW indicates the center well position.

**O. D. is the optical density of the irradiated dosimetry solution.

Note-a This run was made in a thick walled glass vial.

C. Analytical Method

TABLE X

RETENTION TIMES FOR VARIOUS COMPOUNDS

(Fisher-Gulf Partitioner; Stainless Steel Column with Tri-o-tolyl Phosphate; Temperature as specified; Flow rate 110cc Helium/min)

Compound	B. P. °C	Column Temp. °C	Ret. time min
Isopropyl mercaptan	60	100	1.7
n-Propyl mercaptan	68	100	2.3
Toluene	110.6	100	7.0
Isopropyl sulfide	120.4	100	11.0
n-Propyl sulfide	141-2	100	12.5
Propyl disulfide	192	100	33.0
Isobutyl mercaptan	88	120	2.9
n-Butyl mercaptan	98	120	3.3
Toluene	110.6	120	5.7
Isobutyl sulfide	172	120	15.5
n-Butyl sulfide	182	120	28.0

C. Analytical Method (contd)

TABLE XI

CHROMATOGRAPHY STANDARDS AND CALIBRATION

(1) Composition of the Standards:

Std. No.	Weights				Weight %			
	i-M	n-M	T	S	i-M	n-M	T	S
7		2.51	2.44	2.60		33.4	34.4	32.2
8		0.84	2.60	0.81		19.7	61.2	19.1
9		1.27	10.40	1.26		9.8	80.2	9.8
10		2.49	4.32	1.77		29.0	50.4	20.6
12	0.40	3.20	8.58	1.67	3.0	23.0	62.0	12.0
17	0.81	3.30	6.87	1.67	6.4	26.0	54.4	13.2

(2) Analysis:

Std. No.	Chromatogram Percent Area				Analysis Avg., %			
	i-M	n-M	T	S	i-M	n-M	T	S
7		30.8	38.4	30.8		30.8	38.4	30.8
8		18.1	65.2	16.7		18.1	65.2	16.7
9		8.2	84.7	7.1		8.6	84.0	7.4
		9.0	83.3	7.7				
10		31.2	53.8	15.0		30.4	54.0	15.8
		29.6	54.2	16.2				
12	2.3	23.0	64.4	9.3	2.4	23.6	64.1	9.4
	2.5	24.2	63.8	9.5				
17	4.5	27.9	55.0	12.6	4.4	28.1	55.1	12.4
	4.3	28.4	55.2	12.1				

Note: Column numbers 2 to 5 and 6 to 9 stand for iso and n-propyl mercaptans, toluene and normal propyl sulfide respectively. A Fisher-Gulf Partitioner, used to make the analysis, evaluates the area under each peak by an attached integrator.

D. Sample Calculations

Calculations from experimental data;

The method of calculations is illustrated in the following example for run number C11, Table XIV and using values for physical properties from Table VI.

Reactant Charge;

Propylene = Vol. x density x (1/mol.wt.)

= 5cc x .65 gms/cc (1/42.08) = .076 moles

Hydrogen Sulfide = 2.5cc x .99 gms/cc x (1/34.08) = .074 moles

Assuming the volumes to be additive and taking the average moles charged = .075 the concentration of individual reactant =(.075 moles/7.5cc) x 1000 cc/liter = 10 moles/liter.

The total charge in grams = 5cc x .65 gms/cc 2.5cc x .99 gms/cc = 5.70 gms.

Radiation;

Position = 66 cms. Irradiation time = 45 min.

Dosimetry Data: From Table IX, dose rate = 67.2 rads/min

Total dose = 67.2 rads/min x 45 min = 3020 rads

Product Recovery;

Chromatographic Analysis

Propyl Mercaptan (RSH) = 1.187 gms

Propyl Sulfide (RSR) = 0.193 gms

Total Product = 1.38 gms

moles (RSH) = (gms/mol.wt.)=(1.187/76.1)= .01555

moles (RSR) = (gms/mol.wt.) =(0.22/118.2) = .00163

Conc. of mercaptan = .01718/7.5 x 1000 cc/liter

= 2.07 moles/liter

Similarly,

Concentration of sulfide = .00163/7.5 x 1000 = 0.22 moles/liter

$\therefore$ H_2S reacted = X_A = 2.07 + 0.22 = 2.29 moles/liter

Conversion H_2S;

moles H_2S reacted = moles RSH + moles RSR = .01718

Total moles charged = .075

% Conversion = .01718/.075 x 100 = 22.9

Reaction Rates;

The average reaction rate (R_{avg}) is given by dividing the amount of hydrogen sulfide reacted by the time of irradiation

$$R_{avg} = \frac{2.29 \text{ (moles/liter)} H_2S \text{ reacted}}{45 \text{ min.}}$$

$$= 0.051 \text{ moles/(liter)(min)}$$

For Figure 13, various values are obtained as follows:

For run C11 (Note: all concentrations are in (moles/liter)

Initial conc. H_2S = C_{AO} = 10

Final Conc. H_2S = C_A = $C_{AO}-X_A$ = 10 - 2.29 = 7.71

C_{Aavg} = 10 + 7.71/2 = 8.86

Since it it assumed that C_D is negligible (See text) $C_{Bavg} = C_{Aavg} = 8.86$

Hence $X_A/ C_{Aavg}C_{Bavg} \times 10^2 = 2.29 \times 10^2/8.86 \times 8.86$

$= 2.622$ liter/moles

Also,

$\log (R_{avg}/C_{Aavg}C_{Bavg} \times 10^4) \doteq - 3.2336$

$I^{0.5}t = 67.2^{0.5} \times 45 = 369$ and $\log I = 1.8273$

Integrated Rate Expression, (Equation (18) or (19)).

The use of the integrated rate expression (Equation (19)) for calculating the rate constant and also for determining the theoretical amount of time required for specific amount of hydrogen sulfide reacted is illustrated below.

Substituting the values of initial concentrations $C_{AO} = C_{BO} = 10$ moles/liter, amount of hydrogen sulfide reacted $X_A = 2.0$ moles/liter and $\lambda = 9.0$ in Equation(19),

$$t = \frac{1}{k\sqrt{\left\{4C_{AO}C_{BO}-(C_{AO}+C_{BO}+\lambda)^2\right\}}} \ln\left[\frac{2X_A-(C_{AO}+C_{BO}+\lambda)-\sqrt{\left\{4C_{AO}C_{BO}-(C_{AO}+C_{BO}+\lambda)^2\right\}}}{2X_A-(C_{AO}+C_{BO}+\lambda)+\sqrt{\left\{4C_{AO}C_{BO}-(C_{AO}+C_{BO}+\lambda)^2\right\}}} \left\{\frac{-(C_{AO}+C_{BO}+\lambda)+\sqrt{\left\{4C_{AO}C_{BO}-(C_{AO}+C_{BO}+\lambda)^2\right\}}}{-(C_{AO}+C_{BO}+\lambda)-\sqrt{\left\{4C_{AO}C_{BO}-(C_{AO}+C_{BO}+\lambda)^2\right\}}}\right\}\right]$$

Using the value of average reaction rate constant from Table III, $k = 4.39 \times 10^{-4}$ liter/(mole)(min) for propylene-hydrogen sulfide reaction with equimolar reactant composition (mole fraction $C_3H_6 = H_2S = 0.5$) at -78°C and radiation intensity = 30.6 rads/min the theoretical reaction time = 64 minutes.

The initial rate may be obtained from the knowledge of composition at t = o and the rate expression(14),

$$\frac{-d\left[H_2S\right]}{dt} = k(C_{AO}-X_A)(C_{BO}-X_A)-k_rX_A$$

Substituting the value of C_{AO}, C_{BO} and k listed above, and since at $t = o$, $X_A = 0$

$$\frac{-d\left[H_2S\right]}{dt} = .044 \text{ moles/(liter)(min)}$$

The fraction of H_2S reacted is equal to the reaction rate divided by the total initial concentration of all species ($C_{AO}+C_{BO} = 20$ moles/liter)

mole fraction, H_2S reacted/min = $.044/20 = 2.20 \times 10^{-3}$

Normalization of Rates;

The normalization of the rate constant and reaction times as a function of conversion is done as follows.

Since the intensity exponent was found to be 0.5 for intensity between 30.6 and 116.6 rads/min,

$$k_{norm} = k_{act}\left(\frac{I_{norm}}{I_{act}}\right)^{0.5} \quad ; \quad t_{norm} = t_{act}\left(\frac{I_{act}}{I_{norm}}\right)^{0.5}$$

where k_{norm} = normalized rate constant and k_{act} = actual rate constant found at any intensity I_{act} , etc.

Thus from Table XVIII;

$I_{act} = 43.3$; $t_{act} \simeq 60$ minutes for conversion $X_A = 2.54$ moles/liter and $k_{act} = 7.13 \times 10^{-4}$ liter/(mole)(min)

In order to normalize the data to $I_{norm} = 30.6$ rads/min

$$t_{norm} = 60 \times \left(\frac{43.3}{30.6}\right)^{0.5} = 72 \text{ minutes}$$

$$k_{norm} = (7.13 \times 10^{-4}) \times \left(\frac{30.6}{43.3}\right)^{0.5} = 5.99 \times 10^{-4} \text{ liter/(mole)(min)}$$

The average value of the normalized rate constant k(at I = 30.6 rads/min) and the average error may be obtained from the last column in Table XVIII. Thus

$$k = (4.7 \pm 0.9) \times 10^{-4} \text{ liter/(mole)(min)}$$

Secondary Reactions;

From Equation (29), $k_s/k = \left(\frac{\Delta C_D}{\Delta X_A}\right)\left(\frac{C_{Aavg}}{C_{Cavg}}\right)$

From stoichiometry $C_A = C_{AO}-X_A$ and $C_C = X_A-C_D$ and from Table XIV the initial concentration C_{AO} = 10 moles/liter. The simultaneous concentrations C_D and X_A at any time are obtained from Figure 10, and the calculations are listed in Table XX. Thus for the first two points in Table XX (between $X_A = 0$ and 1.0) the following may be calculated (all concentrations are in moles/liter). For $X_A = 1.0$, $C_D = .05$. Hence $C_A = C_{AO}-X_A = 10 - 1 = 9.0$

and $C_C = X_A - C_D = 1 - 0.05 = 0.95$.

Averaging the values for $X_A = 0$ and $X_A = 1.0$,

$C_{Aavg} = (10 + 9)/2 = 9.5$ and $C_{Cavg} = (0 + 0.95)/2 = 0.475$

The increments in X_A and C_D are

$$\Delta X_A = 1 - 0 = 1.0 \text{ and } \Delta C_D = 0.05 - 0 = 0.05$$

Hence

$$k_s/k = (\Delta C_D/\Delta X_A)(C_{Cavg}/C_{Aavg}) = (0.05/1.0)(9.5/0.475) = 0.99$$

Radiation Yield; G-Value

The G-value is defined as the number of molecules changed per 100 ev of energy absorbed. This is calculated as follows for run number C11:

energy absorbed = gms charged x Dose rate (rads/min) x time (min)

$$\times 100 \frac{\text{ergs/gm}}{\text{rads}} \times 6.25 \times 10^{11} \text{ ev/ergs}$$

$$= 5.70 \times 67.2 \times 45 \times 100 \times 6.25 \times 10^{11}$$

molecules reacted = moles reacted x 6×10^{23} (Avogadro's number molecules/mole)

$$= .01718 \times 6 \times 10^{23}$$

Since G-value is equal to the number of molecules reacted per 100 ev;

$$G = \frac{.01718 \times 6 \times 10^{23}}{5.70 \times 67.2 \times 45 \times 100 \times 6.25 \times 10^{11}} \times 100$$

$$= 9.52 \times 10^{5}$$

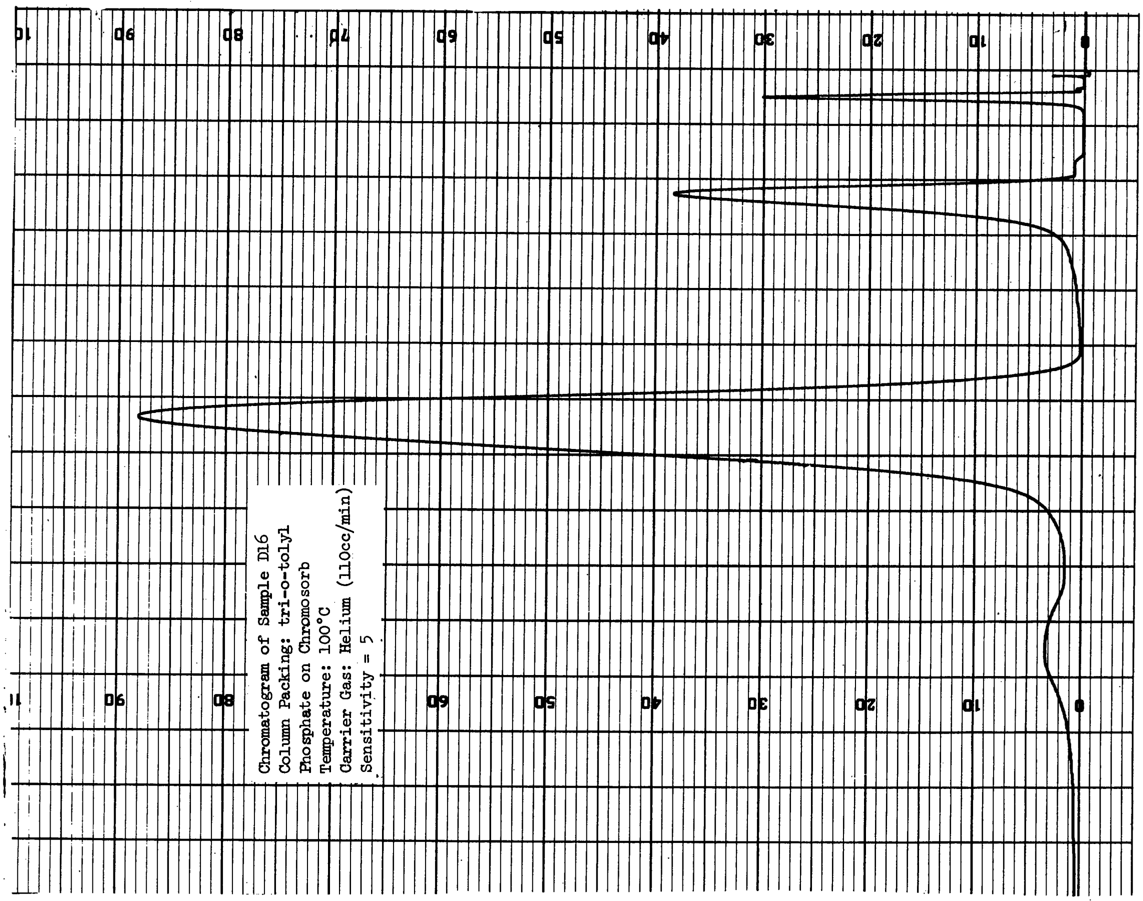
Identification of Reaction Products

The identification and estimation of reaction products by chromotographic analysis is illustrated in the following example.

Run number D16 (Chromatogram shown below)

Chromatographic Peak (excluding air and dissolved gas peaks)	Identification (by comparison with standard sample)	Chromatographic Pips (integrator markings, proportional to area)	Product Weight (gm) (toluene as intl.std)
1	n-propyl mercaptan	18	0.43
2	toluene	104	2.50
3	n-propyl sulfide	4	0.10

The distillation analysis is illustrated in the following example. For run number A24, the first distillate portion was collected between 68°C (B.P. of n-propyl mercaptan) and 120°C, and was identified as n-propyl mercaptan by chromatographic analysis. The second portion of the distillate was identified as n-propyl sulfide together with n-propyl mercaptan. There was no residue left in the flask and no other substances were indicated by this analysis.



Chromatogram of Sample D16
Column Packing: tri-o-tolyl
Phosphate on Chromosorb
Temperature: 100°C
Carrier Gas: Helium (110cc/min)
Sensitivity = 5

E. Tabulated Data

TABLE XII

PROPYLENE-HYDROGEN SULFIDE: PRELIMINARY EXPERIMENTS*

Run No.	Date 1957	$\frac{H_2S}{C_3H_6}$	I $\frac{Krads}{hr}$	Time min	Product Analysis[a] Wt. gms	RSH moles/liter	RSR moles/liter	Hydrogen Sulfide Reacted $\frac{moles}{liter}$	%Conv.	G-Value $(-H_2S)$ x 10^{-4}
A 1	8-17	1.0	40	133	0.83	.38	.17	.55	5.5	0.83
A 2	8-17	1.0	40	240	1.44	.89	.15	1.04	10.4	0.88
A 3	8-15	1.0	40	598	1.06	.52	.19	.71	7.1	0.24
A 4	8-15	1.0	40	899	1.32	.78	.16	.94	9.4	0.21
A 5	8-3	1.0	40	2430	5.58	2.62	1.1	3.72	37.2	0.31
A 6	8-3	1.0	40	2430	3.87	2.29	.46	2.75	27.5	0.23
A 7	6-22	1.0	63	121	4.07	2.10	.67	2.77	27.7	3.07
A 8	6-22	1.0	63	338	5.15	2.94	1.01	3.95	39.5	1.48
A 9	7-16	1.0	63	998	5.69	3.10	1.15	4.25	42.5	0.57
A10	7-16	1.0	63	1458	6.28	2.43	1.02	3.45	34.5	0.27
A11	8-8	1.0	80	30	3.98	2.28	.52	2.80	28.0	9.55
A12	7-31	1.0	80	60	4.56	2.36	.76	3.12	31.2	5.32
A13	7-12	1.0	80	125	5.92	2.49	.41	2.90	29.0	2.37
A14	7-12	1.0	80	125	6.18	1.75	.28	2.03	20.3	1.69
A15	8-8	1.0	80	678	4.03	2.78	1.17	3.95	39.5	0.60
A16	8-8	1.0	80	1920	2.82	3.10	1.1	4.20	42.0	0.22
A17	7-31	1.0	80	125	.31	.21	.02	.23	2.3	0.19
A18	8-20	1.18	40	400	--	----	----	----	----	----
A19	8-20	1.70	40	180	trace	----	----	----	----	----
A20	8-21	1.70	40	243	0.97	.81	.21	1.02	7.5	0.75
A21	8-21	1.70	40	360	1.09	.93	.20	1.13	8.2	0.56
A22	8-22	1.70	40	600	2.90	2.62	.53	3.15	20.9	0.85
A23	8-22	1.63	40	989	0.43	.47	.10	.57	4.2	0.10
A24[b]	8-24	1.70	40	1398	3.20	1.80	.60	2.40	17.3	0.30
A25	8-24	1.68	Dark	7200	No Reaction		----	----	----	----

*All the runs listed in this table were made with technical grade of hydrogen sulfide.

Run A-1 through A-17 were conducted with equimolar reactant composition.

The composition was varied for other runs as indicated.

Moles charged for mole ratio = 1.0; $C_3H_6=H_2S=0.169$.

Moles charged for mole ratio > 1.0; C_3H_6 0.10 to 0.17.

Temperatures = -78°C.

Note-a RSH and RSR indicate no-propyl mercaptan and n-propyl sulfide respectively.

Note-b Reactor irradiated after breaking vacuum subsequent to loading of reactants, so that oxygen was present.

TABLE XIII

PROPYLENE-HYDROGEN SULFIDE: HIGH INTENSITY IRRADIATIONS

Run No.	Date 1961	Intensity raas/min	Time min	Product Analysis Wt. gms	RSH moles/liter	RSR moles/liter	Hydrogen Sulfide Reacted moles/liter	%Conv.	G-Value $(-H_2S)$ x 10^{-4}
B 1	5-26	1570[a]	25	1.46	2.06	0.33	2.39	23.9	7.74
B 2	5-16	1570	60	1.94[d]	--	--	--	--	--
B 3	5-21	1570	75	2.06	2.77	0.78	3.55	35.5	3.83
B 4	5-26	830[b]	25	1.50	--	--	--	--	--
B 5	6-6	830	25	1.59	2.09	0.45	2.54	25.4	15.30
B 6	5-26	830	75	1.85	2.48	0.70	3.18	31.8	6.40
B 7	5-27	830	75	1.92	2.58	0.72	3.30	33.0	6.64
B 8	5-27	365	15	.92	1.49	0.20	1.69	16.9	38.80
B 9	6-6	365	25	1.08	1.87	0.17	2.04	20.4	28.10
B10	7-12	365	75	1.21	1.82	0.34	2.16	21.6	9.94
B11	5-12	1570	25	.74[c]					
B12	5-12	1570	30	.54[c]					
B13	5-12	1570	60	1.94[d]					
B14	5-12	1570	80	1.88[d]					
B15	5-16	830	25	1.18[d]					
B16	5-16	830	30	.91[d]					
B17	5-16	830	60	1.79[d]					
B18	5-16	830	80	1.27[c]					
B19	5-21	135	30	1.38	2.08	0.21	2.29	22.0	71.3
B20	5-21	135	35	1.37	1.78	0.39	2.17	21.7	58.0
B21	5-21	135	40	1.42	2.08	0.26	2.34	23.4	54.5

Equimolar Reactant Composition; Concentration, $C_{AO}=C_{BO}=10$ moles/liter.

Moles charged; $H_2S=C_3H_6=.075$.

Total Volume of Reaction Mixture = 7.5 cc.

Temperature = -78°C.

Note-a Irradiation in the center well of the source.

Note-b Irradiation on the center plane and on the immediate outside of the source cage (C-ring) position.

Note-c The product was not completely recovered.

Note-d The product was not analyzed.

TABLE XIV

PROPYLENE-HYDROGEN SULFIDE: LOW INTENSITY IRRADIATIONS

Run No.	Date 1961	Intensity rads/min	Time min	Product Analysis			Hydrogen Sulfide		
				Wt. gms	RSH moles/liter	RSR moles/liter	Reacted moles/liter	%Conv.	G-Value $(-H_2S)$ x 10^{-5}
C 1	6-6	116.6	15	.70	1.0	.10	1.10	11.0	7.92
C 2	7-12	116.6	30	1.30	2.0	.14	2.14	21.4	7.70
C 3	7-12	116.6	50	1.43	2.2	.19	2.39	23.9	5.16
C 4	6-6	116.6	60	1.51	2.14	.33	2.47	24.7	4.44
C 5	7-12	116.6	120	1.52	2.13	.34	2.47	24.7	2.22
C 6	7-21	67.2	15	.45	0.88	--	.88	8.8	12.40
C 7	7-21	67.2	30	.98[a]	---	--	---	--	---
C 8	12-25	67.2	30	1.01	1.59	.11	1.70	17.0	10.60
C 9	7-17	67.2	30	.99	1.49	.11	1.60	16.0	9.97
C10	11-17	67.2	35	1.21	1.75	.24	1.99	19.9	10.60
C11	7-21	67.2	45	1.38	2.07	.22	2.29	22.9	9.52
C12	10-30	67.2	110	1.54	2.63	.23	2.86	28.6	4.86
C13	8-8	43.3	15	.34	.44	--	.44	4.4	8.49
C14	11-17	43.3	20	.645	1.08	.03	1.11	11.1	16.10
C15	12-25	43.3	30	.818	1.26	.11	1.37	13.7	13.20
C16	8-8	43.3	30	.805	1.20	.14	1.34	13.4	12.90
C17	11-17	43.3	45	1.18	1.76	.26	2.02	20.2	13.00
C18	12-27	43.3	60	1.55	2.28	.28	2.54	25.4	12.30
C19	8-8	30.6	15	.11	.20	--	.20	2.0	5.47
C20	11-17	30.6	20	.30	.52	--	.52	5.2	10.70
C21	8-8	30.6	30	.75	1.23	.05	1.28	12.8	17.50
C22	11-17	30.6	45	1.10	1.69	.16	1.85	18.5	16.90
C23	12-28	30.6	60	1.48	2.20	.25	2.45	24.5	16.80

Equimolar Reactant Composition; Concentration, $C_{AO}=C_{BO}=10$ moles/liter.
Moles charged; $H_2S=C_3H_6=.075$.
Total Volume of Reaction Mixture = 7.5 cc.
Temperature = -78°C.
Note-a Sample Analysis not obtained because of loss of sample.

TABLE XV

PROPYLENE-HYDROGEN SULFIDE: DARK RUNS AND LONG-TIME IRRADIATIONS

Run No.	Date	Intensity rads/min	Time min	Product Analysis Wt. gms	 RSH moles/liter	 RSR	Hydrogen Sulfide Reacted moles/liter	 %Conv.	 G-Value $(-H_2S)$ x 10^{-5}
A. Dark Runs									
CD1	4-3-62	Dark	1800	no product					
CD2	4-3-62	"	1800	"	"				
B. Long Time Irradiations									
CL1	12-7-61	116.6	120	1.52	2.13	.34	2.47	24.7	2.22
CL2	12-27-61	43.3	170	1.48	2.12	.31	2.43	24.3	4.14
CL3	12-28-61	30.6	240	1.76	2.41	.43	2.86	28.4	4.90
CL4	8-16-62	30.6	360	1.40	1.92	.17	2.09	21.0	2.38
CL5	1-26-62	30.6	480	1.80	2.12	.68	2.80	28.0	2.40
CL6	1-25-62	30.6	600	1.89	2.49	.53	3.02	30.2	2.07

C. Discarded Runs (for indicated reasons)

Run No.	Date	Intensity rads/min	Time min	Wt. gms		Remarks
CF1	1-62	Low Intensity Irradiations between 30.6 and 116.6 rads/min. Eight runs in each series.				Vacuum system faulty
CF2	4-62					Propylene cylinder changed
CF3	4-62					H_2S cylinder changed
CF4	6-62					Vacuum system refabricated
CF5	7-11-62	67.2	60	1.14)	Note-a	
CF6	7-17-62	43.3	60	.94)		
CF7	7-17-62	30.6	60	.90)		

Equimolar Reactant Composition; Concentration, $C_{AO}=C_{BO}=10$ moles/liter.
Moles charged; $H_2S=C_3H_6=.075$.
Total Volume of Reaction Mixture = 7.5 cc.
Temperature = -78°C.
Note-a Incomplete Recovery of Product.

TABLE XVI

PROPYLENE-HYDROGEN SULFIDE: VARIABLE COMPOSITION

Run No.	Date	Mole Ratio $C_3H_6:H_2S$	Time min	Product Analysis			Hydrogen Sulfide		
				Wt. gms	RSH moles/liter	RSR	Reacted moles/liter	%Conv.	G-Value $(-H_2S)$ x 10^{-5}
D 1	8-8-61	2.0	20	.16	.29	--	.29	4.8	6.45
D 2	11-17	2.0	40	.55	.87	.06	.93	15.5	10.30
D 3	11-17	2.0	60	.79	1.13	.17	1.30	21.7	9.66
D 4	8-8	2.0	60	.74	1.08	.14	1.22	20.2	9.03
D 5	12-29	2.0	80	1.34	1.58	.50	2.08	34.7	11.60
D 6	12-27	0.5	20	.19	.19	--	.19	1.3	3.67
D 7	12-25	0.5	40	.48	.66	--	.66	4.4	6.37
D 8	12-25	0.5	60	.76	1.25	.04	1.29	8.7	8.30
D 9	12-29	0.5	60	.73	1.20	.05	1.25	8.4	8.03
D10	12-27	0.5	100	1.58	2.53	.15	2.68	17.9	10.34
D11	8-10-62	4.0	30	.100	.17	--	.17	5.6	2.88
D12	8-21	4.0	30	.208	--	--	--	--	--
D13	8-17	4.0	45	.33	.54	.03	.57	18.4	6.41
D14	8-17	4.0	50	.34	--	--	--	--	--
D15	8-10	4.0	60	.49	.62	.15	.77	24.8	6.47
D16	8-21	4.0	75	.53	.76	.11	.87	27.9	5.87
D17	8-21	4.0	120	.90	.92	.43	1.35	43.3	5.67
D18	8-28	0.25	30	trace					
D19	8-23	0.25	65	.30	.52	--	.52	2.7	2.90
D20	8-28	0.25	90	.42	.74	--	.74	4.0	2.98
D21	8-28	0.25	120	.72	1.26	--	1.26	6.6	3.81
D22	8-28	0.25	285	.74	1.30	--	1.30	6.7	1.65

Amount of H_2S charged; 0.045, 0.11, 0.023 and 0.145 moles for mole ratio $C_3H_6:H_2S$ = 2, 0.5, 4 and 0.25 respectively. The equivalent concentration of $H_2S(C_{AO})$ are 6.0, 15.0, 3.1 and 19.3 moles/liter respectively.
Total Volume of Reaction Mixture = 7.5 cc.
Temperature = -78°C. Intensity = 30.6 rads/min.

TABLE XVII

PROPYLENE-HYDROGEN SULFIDE: VARIABLE TEMPERATURE

Run No.	Date	Temp. °C	Time min	Product Analysis Wt. gms	RSH moles/liter	RSR	Reacted moles/liter	%Conv.	G-Value $(-H_2S)$ x 10^{-5}
E 1	12-27-61	-65	15	.12	.21	--	.206	2.1	5.63
E 2	12-27-61	-65	35	.61	1.08	--	1.08	10.8	12.70
E 3	12-29-61	-65	50	1.1	1.70	.15	1.85	18.5	15.20
E 4	12-29-61	-65	100	1.50	2.12	.32	2.44	24.4	10.00
E 5	1-6-62	-25	15	trace					
E 6	1-6-62	-25	30	.81	1.26	.10	1.36	13.6	18.60
E 7	1-6-62	-25	70	.71	1.25	--	1.25	12.5	7.36
E 8	8-31-61	-25	Note-a						
E 9	8-31-61	-25	45	.70	1.14	.06	1.20	11.9	10.90
E10	8-16-63	-78	Note-a						
E11	8-16-63	-25	60	1.08	1.51	.25	1.76	17.6	12.00
E12	8-16-63	-25	60	0.50	.88	--	.88	8.8	6.04
E13	8-18-63	-25	90	0.64[b]	--	--	--	--	--
E14	8-18-63	-25	30	0.52[c]	0.91	--	0.91	9.1	12.50

Equimolar Reactant Composition; Concentration, $C_{A0}=C_{B0}=10$ moles/liter.
Moles charged; $H_2S=C_3H_6=.075$.
Total Volume of Reaction Mixture = 7.5 cc.
Temperature = -78°C; Intensity = 30.6 rads/min.
Note-a The vials for these experiments were accidentally broken
Note-b The product was not completely recovered
Note-c The product was not analyzed because of loss of sample. The calculations were made assuming RSH as the only product.

TABLE XVIII

PROPYLENE-HYDROGEN SULFIDE: NORMALIZED VALUES OF LOW INTENSITY DATA TO I=30.6 RADS/MIN

Intensity rads/min	Time min	Conversion mole/liter	Calculated k(x10^4) liter/(mole)/(min)	Normalized* (to I=30.6) Time min	Normalized* (to I=30.6) k(x10^4)** liter/(mole)/(min)
30.6	15	0.2	1.40	15	1.40
30.6	20	0.52	2.82	20	2.82
30.6	30	1.28	5.27	30	5.27
30.6	45	1.85	5.75	45	5.75
30.6	60	2.45	6.70	60	6.70
43.3	15	0.44	3.23	18	2.72
43.3	20	1.11	6.77	24	5.70
43.3	30	1.37	5.75	36	4.84
43.3	30	1.34	5.63	36	4.74
43.3	45	2.02	6.55	54	5.50
43.3	60	2.54	7.13	72	5.99
67.2	15	0.88	6.83	22.5	4.62
67.2	30	1.70	7.65	45	5.16
67.2	30	1.60	7.06	45	4.77
67.2	35	1.99	8.30	52	5.60
67.2	45	2.29	7.90	67	5.34
116.6	15	1.10	8.80	29.5	4.50
116.6	30	2.14	10.70	59	5.50
116.6	50	2.39	7.70	98	3.94
116.6	60	2.47	6.80	118	3.48

* The normalized values were obtained by multiplying the reaction times by a factor of $(I/30.6)^{0.5}$ and the rate constants by $(30.6/I)^{0.5}$, where I = intensity of radiation and 30.6 (rads/min) represents the intensity to which the data is normalized.

**The average value of the rate constant k obtained from this data, after discarding the 15 minute points for radiation intensity of 30.6 and 43.3 rads/min, is (5.0 ± 0.7) x 10^{-4} liter/(mole)(min).

TABLE XIX

PROPYLENE-HYDROGEN SULFIDE; CALCULATED VALUES OF AVERAGE REACTION RATES

(Experimental Data - Table XIV; H_2S Reacted (X_A) ≃ 1.0 to 2.5 moles/liter)

I rads/min	Time(t) min	X_A moles/liter	(a) (See notes below)	(b)	$I^{0.5}t$	logI	(c)
30.6	30	1.28	1.46	4.90	165	1.486	-3.310
30.6	45	1.85	2.25	5.00	248	1.486	-3.301
30.6	60	2.45	3.18	5.30	330	1.486	-3.276
43.3	30	1.37	1.58	5.28	198	1.636	-3.277
43.3	30	1.34	1.54	5.13	198	1.636	-3.290
43.3	45	2.02	2.50	5.55	297	1.636	-3.256
43.3	60	2.54	3.32	5.54	396	1.636	-3.256
67.2	15	0.88	0.96	6.43	123	1.827	-3.192
67.2	30	1.70	2.03	6.77	246	1.827	-3.169
67.2	30	1.60	1.89	6.30	246	1.827	-3.201
67.2	35	1.99	2.48	7.07	287	1.827	-3.151
67.2	40	2.29	2.62	5.84	369	1.827	-3.234
116.6	15	1.10	1.23	8.22	162	2.066	-3.035
116.6	30	2.14	2.68	8.95	324	2.066	-3.048

Note-a Column lists values of $(1/C_{Aavg}C_{Bavg})\ X_A(x10^2)$
Since C_{A0} = 10 moles/liter and $C_A = C_B = C_{A0}-X_A$ (See Page 45)
$C_{Aavg} = \{C_{A0} + (C_{A0}-X_A)\}/2$

Note-b Column lists values of $(R_{avg}/C_{Aavg}C_{Bavg})$ x 10^4 where
$R_{avg} = \Delta X_A/\Delta t = X_A/t$ Iinitial average rate with $X_A = 0$ at $t = 0$)

Note-c Column lists logarithms of numbers in column (b).

TABLE XX

PROPYLENE HYDROGEN SULFIDE: CALCULATED VALUES FOR SECONDARY REACTIONS

Mole Ratio***	X_A	C_D	C_A	C_C	C_{Aavg}	C_{Cavg}	C_D	X_A	k_s/k**
A. Data interpolated from Figure 10.*									
1:1	0	0	10.0	0					
	1.0	0.05	9.0	0.95	9.5	0.48	0.05	1.0	0.99
	1.5	0.12	8.5	1.38	8.75	1.16	0.07	0.5	1.10
	2.0	0.20	8.0	1.80	8.25	1.60	0.08	0.5	0.78
	2.5	0.32	7.5	2.18	7.75	1.99	0.12	0.5	0.96
B. Data interpolated from Figure 15.									
4:1	0	0	3.1	0					
	0.6	0.06	2.5	0.54	2.8	0.27	0.06	0.6	1.04
	0.8	0.15	2.3	0.65	2.4	0.60	0.09	0.2	1.80
	1.0	0.25	2.1	0.75	2.2	0.70	0.10	0.2	1.57
	1.2	0.35	1.9	0.85	2.0	0.80	0.10	0.2	1.25
2:1	0	0	6.0	0					
	1.0	.075	5.0	0.925	5.5	0.46	.075	1.0	0.90
	1.2	0.14	4.8	1.06	4.9	0.99	.065	0.2	1.60
	1.4	0.21	4.6	1.19	4.7	1.11	.07	0.2	1.50
	1.6	0.28	4.4	1.32	4.5	1.25	.07	0.2	1.26
	1.8	0.37	4.2	1.43	4.3	1.38	.09	0.2	1.40
	2.0	0.46	4.0	1.54	4.1	1.49	.09	0.2	1.24
1:2	0	0	15.0	0					
	1.6	0.07	13.4	1.53	14.2	0.76	.07	1.6	0.82
	2.6	0.15	12.4	2.45	12.9	1.99	.08	1.0	0.52

*C_A, C_C, C_D -- Concentration (moles/liter) of hydrogen sulfide, propyl mercaptan and propyl sulfide respectively.
X_A denotes H_2S reacted (moles/liter)
Note; $C_A=C_{A0}-X_A$, $C_C=X_A-C_D$
The subscript 'avg' denotes average concentration over any interval (average of two successive horizontal columns)
Δ denotes difference between the initial and final concentration over any interval.

**k_s/k represent the ratio of rate constant for secondary reaction and primary reaction (Equation (29)).

***Ratio of concentrations of propylene and hydrogen sulfide.

TABLE XXI

BUTENE-HYDROGEN SULFIDE IRRADIATIONS

Run No.	Date	Hydrocarbon	Time min	Product Analysis[a] Wt. gms	RSH moles/liter	RSR	Hydrogen Sulfide %Conv.	G-Value $(-H_2S)$ $\times 10^{-3}$
F 1[b]	1-1-62	Butene-1	60	no reaction				
F 2[b]	1-1-62	"	60	no reaction				
F 3	1-2-62	"	120	0.177	0.23	--	2.63	1.62
F 4	1-2-62	"	220	0.213	0.28	--	3.17	1.07
F 5	1-4-62	"	540	0.659	0.82	.03	9.57	1.33
F 6	1-2-62	"	720	0.986	1.08	.13	13.70	1.42
F 7	8-16-63	"	360	0.423	0.55	--	6.27	1.29
F 8[c]	1-1-62	Butene-2	60	--	--			
F 9	1-2-62	"	15	0.517	0.67	--	7.65	37.70
F10	1-4-62	"	60	1.60	2.05	.03	23.60	29.30
F11	1-2-62	"	120	2.10	2.19	.34	28.70	17.80
F12	8-18-63	"	60	1.924	2.33	.11	27.70	40.00
F13	1-2-62	Isobutene	30	0.155	0.20	--	2.30	5.58
F14	1-4-62	"	60	0.372	0.48	--	5.50	6.76
F15	1-2-62	"	120	1.18	1.54	--	17.50	10.80
F16	1-4-62	"	180	1.50	1.92	--	22.00	8.96
F17	1-30-62	"	90	1.396	1.82	--	20.70	17.10
F18	1-30-62	"	300	3.13	2.34	1.08	38.70	9.63
F19	8-16-63	"	60	0.33	0.43	--	4.88	6.00
F20	8-16-63	"	360	2.91	3.41	.23	41.30	8.54

Equimolar Reactant Composition; Concentration, $C_{A0}=C_{B0}=8.8$ moles/liter.
Moles charged, $H_2S=C_3H_6=.075$.
Total Volume of Reaction Mixture = 8.5 cc.
Temperature = -78°C; Intensity = 1330-1570 rads/min.

Note-a The RSH and RSR have structures of normal, secondary and iso- for butene-1,-2 and isobutene respectively.

Note-b Experiments F1 and F2 were conducted at Intensity = 30.6 and 43.3 rads/min. respectively.

Note-c During the experiment the vacuum was lost.

X. NOMENCLATURE

Basic Symbols

A°U.	Angstrom Units
C	Concentration of any specie indicated by a subscript; also designated by putting component in brackets, i.e. C_3H_6 , (moles/liter)
ΔC	Incremental difference in concentration over a specified interval of time (Δt) etc.
C_A	Concentration of hydrogen sulfide (moles/liter)
C_{AO}	Initial concentration of hydrogen sulfide (moles/liter)
C_{Aavg}	Average concentration of hydrogen sulfide (over a specified interval), (moles/liter)
C_B	Concentration of hydrocarbon (propylene, butene-1, etc. as indicated by context)(moles/liter)
C_{BO}	Initial concentration of hydrocarbon (moles/liter)
C_{Bavg}	Average concentration of hydrocarbon (propylene, butene-1, etc. as indicated by context)(moles/liter)
C_C	Concentration of mercaptan formed as a reaction product, corresponding to the hydrocarbon i.e. n-propyl mercaptan for propylene-hydrogen sulfide system
C_D	Concentration of sulfide formed as a reaction product, corresponding to the hydrocarbon i.e. n-propyl sulfide for propylene-hydrogen sulfide reaction
G	Molecules converted per 100 electron volts absorbed
ΔH_A	Activation energy (cal/mole)
I	Intensity of radiation or dose rate; rads/min
K	Equilibrium constant for formation of $\dot{C}_3H_7S$ radical
k	Reaction rate constant for forward reaction (Equation (9) (11))
k'	Reaction rate constant defined by Equation (20)
k''	Reaction rate constant defined by Equation (95)
k_1-k_7	Rate constants for various steps in the proposed chain mechanism - Page 71

NOMENCLATURE (CONT'D)

Other Symbols

The following notations were used for arbitrary groupings of constants and factors such as concentrations to facilitate the handling of various expressions.

A	$k_3[C_3H_6]$
A'	$k_3k_4\sqrt{2k_1(I)}$
a_1	$B' - 2\phi\sqrt{B'C'} + C'$
a_2	$2\phi\sqrt{B'C'} - C'$
B	$k\,[H_2S]$
B'	$k_3^2k_5$
C	k_5
C'	$k_4^2k_7$
D	k_7
E	$k_6 = \phi\sqrt{k_5k_7}$
F	$k_1(I)$
G	$k_2[H_2S]$
p	$C_{AO}C_{BO}$
q	$4C_{AO}C_{BO} - (C_{AO} + C_{BO} + \lambda)$
r	$(C_{AO} + C_{BO} + \lambda)$
X	Concentration of radical - $[\dot{C}_3H_7S]$
Y	Concentration of radical - $[HS\cdot]$
Z	Concentration of radical - $[H\cdot]$

NOMENCLATURE (CONT'D)

k_{avg}	Reaction rate constant defined by Equation 21
k_r	Reaction rate constant for reverse reaction (Equation (9), (11))
k_s	Reaction rate constant for secondary reaction (Equation (10), (27))
M/N	Ionic yield - number of molecules reacted per ion-pair formed
n	Intensity exponent in the expression relating reaction rate and intensity
PRF	Phoenix Radiation Facility
R	Reaction rate (moles/liter min) or (mole fraction, hydrogen sulfide reacted/min) also used to denote organic radicals
T	Temperature (°C or °K)
t	Time (min or hr)
W	Mean energy required to form ion-pair; electron volts (ev)
x	Thickness of absorbing material (cm.)
x_A	Hydrogen sulfide reacted (moles/liter)
Δx_A	Incremental difference in the amount of hydrogen sulfide reacted over a specified interval (moles/liter)

Greek Letters

α	Mole fraction H_2S in reaction mixture
β	Mole fraction C_3H_6 in reaction mixture
ϵ	Molar extinction coefficients for Fe^{+++} ions (for optical measurements)
θ	Time interval - radioactive decay (years)
κ	Coefficient for energy absorption by pair-production
λ	Ratio of rate constants, k_r/k
μ	Linear energy absorption coefficient; also used for mathematical treatment of rate equation and is defined by Equation 93
σ	Coefficient for energy absorption by Compton effect
τ	Coefficient for energy absorption by photo-electric effect
φ	Ratio of rate constants, $k_6 / \sqrt{k_5 k_7}$

NOMENCLATURE (CONT'D)

Symbols for Transient Species

. (dot)	The dot is used to represent an odd electron characterizing a free radical. The placement of the dot indicates the active center; e.g., in $HS\cdot$, the sulfur atom possesses an odd electron, while in $\dot{C}_3H_7S$ a carbon atom possesses an odd electron.
*	The star is used as a superscript to denote an excited molecule, e.g. AB^*.
+, -	Charged molecules are denoted by the + or - sign; e.g. AB^+ - positive ion, AB^- - negative ion.
$\rightsquigarrow$	This type of an arrow designates the impact of a photon, denoted as $h\nu$.
'(prime)	The primes are used as superscripts for arbitrary separation of various symbols (as in A, A') or of radicals (as in R, R'); it is also used to denote a derivative (as in $R' = dR/d\alpha$).

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