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METHANETHIOL-OLEFIN ADDITION AND CO-OXIDATION

by

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of the requirements for the degree of
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ABSTRACT

The kinetics of the photo-initiated addition and co-oxidation reactions of the methanethiol-olefin system have been investigated in the gas phase, primarily for the purpose of determining relative reactivities of olefins towards thiyl radicals.

The addition of methanethiol to butadiene was found not to be a chain reaction which is in contrast to the addition to mono-olefins, where long chain lengths have been observed; this is due to the fact that the adduct radical formed from butadiene is unreactive, and as a result no rate constants could be determined. But due to the irreversibility of addition, butadiene was found to inhibit the thiyl radical isomerization of cis-butene-2. From the inhibition kinetics the rate constant for CH_3S attack on butadiene was found to be 6.8×10^7 liter mole^{-1} sec^{-1}. The inhibition technique appears useful as a general method for determining attack constants for conjugated olefins.

The addition of thiyl radicals to acetylene was found to be reversible at 25°C which results in an overall negative activation energy. The rate of dehydrogenation of thiol by adduct radicals was found to be competitive with the decomposition rate of adduct radicals. From the resulting rate expression, the rate constant for CH_3S attack on acetylene was found to be 4.8×10^5 liter mole^{-1} sec^{-1} which is

about 6 times less than the attack constant determined for ethylene.

The co-oxidation reaction was examined for the purpose of determining CH_3S attack constants for mono-olefins since the kinetics of addition to mono-olefins gives only rate constant ratios. The mechanism postulated for co-oxidation of methanethiol and olefins is analogous to that for addition except that now oxygen reacts irreversibly with adduct radicals, thus competing against the decomposition of adduct radicals. The rate constant for the reaction of adduct radicals with oxygen was found to be very fast ($\sim 10^9$ liter mole^{-1} sec^{-1}). From the ratio of rate constants for the competing reactions of adduct radicals, it was possible to establish conditions under which the reversibility of thiyl radical addition becomes negligible. Under such conditions, by the simultaneous co-oxidation of several olefins, the relative reactivities of the following olefins were determined to be: ethylene, 1.000; methylacetylene, 0.92; trans-butene-2, 1.96; allene, 2.24; propylene, 2.42; cis-butene-2, 4.13; and isobutene, 4.45; where the addition to ethylene was arbitrarily taken as unity. The co-oxidation technique represents an entirely new approach to the problem of relative reactivities and appears promising as a general method for determining the reactivity of all olefins towards thiyl radicals.

ACKNOWLEDGEMENTS

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INTRODUCTION

The present investigation of the photo-initiated addition and co-oxidation of methanethiol and olefins in the gas phase was undertaken primarily to determine the relative reactivity of different olefins towards thiyl radicals and to correlate these reactivities with structural properties of the reactants. Much attention was directed towards the details of the reaction mechanism which proved vital in the development of several new techniques for the determination of relative reactivities.

Most of the early work on the addition of thiols to olefins (1-6) has been concerned primarily with the identification of products. Since comprehensive review articles covering this aspect are currently available (7,8), the present discussion will only include some general features. Ashworth and Burkhardt (1) were the first to observe that thiols add to olefins in an anti-Markownikoff manner, and Burkhardt (2) suggested that free radicals were involved. The generally accepted radical chain mechanism was proposed later by Kharasch and co-workers (3). In general, thiyl radicals will attack unsymmetrically substituted double bonds at the carbon which results in the more stable of the two possible intermediate radicals. The intermediate radical then abstracts hydrogen from thiol to form a thioether and a new thiyl radical, thus continuing the chain.

INTRODUCTION

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The kinetics of the free radical addition of thiyl radicals, RS, to olefins has been studied (9-17) in this laboratory and elsewhere. The most recent investigations of the addition of methanethiol to olefins in the gas phase (18-24) have shown that the reaction is a chain process of considerable length involving the following addition and chain transfer steps:

$$RS + CH_2{=}CHR' \underset{k_3}{\overset{k_1}{\rightleftharpoons}} RSCH_2\text{-}CHR' \qquad \text{(1) and (3)}$$

$$RSCH_2\text{-}CHR' + RSH \xrightarrow{k_2} RSCH_2\text{-}CH_2R' + RS \qquad \text{(2)}$$

Overall negative activation energies of 8 to 9 kcal have been obtained for the addition of methanethiol to a series of olefins (18, 19) which has lead to the conclusion that the addition occurs reversibly (reaction 3). This reversibility was also demonstrated by the much faster isomerization of cis- to trans-butene-2 during the addition reaction (15,20). In view of this reversibility and the fact that a first order dependence of the rate on both thiol and olefin was obtained, it was concluded that the rate expression for addition contained a complex function of the rate constants, k_1, k_2, and k_3. Consequently the actual rate of addition of thiyl radicals to olefins (reaction 1) is not equal to the rate of product formation and therefore the attack constant, k_1, cannot be obtained directly from the rate of addition.

In spite of these obvious complications, Walling and Helmreich (25) have reported the relative reactivities of various olefins towards dodecanethiol at 60°C by following the relative disappearance of olefin under competitive conditions. Since it was assumed that the addition was irreversible, the rate constants are questionable at best. Their work has been summarized in a recent review article (26).

A much more intensive study by Graham, Mieville, and Sivertz (24) in the gas phase has been made on the isomerization of butene-2 and 1,2-ethylene-d_2 which occurs during methanethiol addition. Initiation was carried out by the ultraviolet photolysis of methanethiol and the rate of initiation was obtained by measuring the evolution of hydrogen by means of a mass spectrometer. Careful consideration was given to the energetics of the reaction, since the adduct radical formed by reaction 1 initially contains the exothermic heat of reaction, which has been estimated by Franklin's method (27) to be about 18 kcal for butene-2. The rate of isomerization was found to be independent of pressure above 4 torr of reactants at 25°C, indicating that isomerization above this pressure occurs by the unimolecular decomposition of a thermally equilibrated adduct radical. The isomerization kinetics were found to be first order with respect to olefin and zero order with respect to thiol, from which the rate constant for the attack step, k_1, was found to be 2×10^6 and 4.8×10^5 liter mole^{-1} sec^{-1} for butene-2 and ethylene-d_2, respectively. In both cases, the overall activation energy for isomerization was found to be close to zero (E_a= 0.050 ± 0.046 kcal) which means that the addition of thiyl radicals to these olefins (reaction 1) has zero activation energy; the same is probably true for other olefins.

Graham et al.(24) have also carried out a detailed kinetic analysis of the addition of methanethiol to ethylene, propylene, and butene-2 in the gas phase and observed overall negative activation energies of 5.3, 7.0, and 11.7 kcal, respectively. Their work clearly demonstrates the inherent difficulty in obtaining relative reactivities of olefins towards thiyl radicals from relative rates of addition. For instance, at 25°C and under identical conditions, the thiyl attack constant for butene-2 is several times greater than that for ethylene, yet the overall rate of addition is greater for ethylene. The reason for this situation is that the ratio of rate constants, k_1k_2/k_3, which governs the rate of addition is greater for ethylene than for butene-2. It was suggested, that under the proper conditions, i.e. at high thiol concentrations and low temperatures, all the intermediate adduct radicals would transfer with thiol (reaction 2) rather than dissociate (reaction 3). Under such conditions the reversibility of the initial attack step would become negligible, and hence the technique of obtaining relative reactivities from relative rates of addition would be valid. Unfortunately, these conditions are limited by the vapour pressure of methanethiol and by the problem of non-uniform absorption of light by thiol. Even with these difficulties, the possibility of obtaining absolute rate constants for thiyl addition to olefins from the study of individual reaction systems appears quite promising.

It is of considerable interest to compare the addition of hydrogen bromide to olefins with that of thiols since bromine atoms are even more electrophilic than thiyl radicals. Armstrong and Spinks (29) have investigated the gamma-ray initiated addition of HBr to ethylene and found a reaction mechanism analogous to that of thiol addition with the following propagating steps:

$$CH_2{=}CH_2 + Br \underset{k_3}{\overset{k_1}{\rightleftharpoons}} CH_2{-}CH_2Br \qquad (1)\text{ and }(3)$$

$$CH_2{-}CH_2Br + HBr \xrightarrow{k_2} CH_3{-}CH_2Br + Br \qquad (2)$$

which result in the formation of ethylbromide. Both reaction 1 and reaction 2 are exothermic by about 8 and 10 kcal, respectively; reaction 1 probably has zero activation energy while the activation energy for reaction 2 may be estimated to be about 4 kcal.

The addition of Br to olefins also occurs reversibly. This possibility has been suggested by several workers (29,30) but the work of Oldershaw and Cvetanovic (31) demonstrates the reversibility most convincingly; the isomerization of butene-2 and ethylene-d_2 occurs about a hundred times faster than the formation of addition products. Since the rate of isomerization was so high that initial rates could not be measured it was believed that energy-rich radicals were involved but conclusive evidence could not be obtained. In any event, the addition of bromine atoms to olefins appears to be even more reversible at room temperature than that of thiyl radicals.

Nevertheless, an attempt was made by Abell (32) to determine the relative reactivity of a series of olefins towards bromine atoms in the gas phase by following the relative rates of bromide formation under competitive conditions. The situation was almost identical to that encountered during the addition of thiols to olefins: a rapid cis-trans isomerization of the unreacted olefin and an overall negative activation energy for addition. This clearly indicates that the initial attack occurs reversibly which unfortunately precludes the possibility of obtaining meaningful results by such methods. Therefore, relative reactivities of olefins towards bromine atoms obtained by such methods are also questionable. In view of these complications it appears that the kinetics of the addition of bromine atoms to olefins requires further consideration.

Several interesting conclusions may be drawn from the stereochemistry of the addition of methanethiol and hydrogen bromide to olefins. Both CH_3SD and DBr add to cis- and trans-butene-2 at room temperature in a non-stereospecific manner. But at low temperatures (-78°C) the addition of DBr to butene-2 occurs stereospecifically to form the threo-bromide from cis-butene-2 and the erythro-bromide from trans-butene-2 (33). On the other hand, the addition of CH_3SD to butene-2 is non-stereospecific at -70°C, but when the addition was carried out in the presence of DBr, stereospecific products were obtained: the threo-sulfide from the trans isomer and the erythro-sulfide from the cis isomer (34).

From a consideration of the stereochemistry discussed above, Skell (35) has suggested two possible structures for the intermediate radicals formed during the addition of both bromine atoms and thiyl radicals. The first, by recognizing that DBr is a very rapid transfer agent, is that classical radicals are involved; the rate of deuterium-atom transfer from DBr to the intermediate radical being faster than the internal rotation between the different conformations. The second possibility is the initial formation of a bridged radical (or π-complex) which isomerizes to a classical radical; in this case DBr transfers fast enough to intercept the bridged radical. However, with present data, it is almost impossible to distinguish between these two cases. But Skell (36) has obtained additional stereochemical evidence of bridged radicals for bromine atoms; the radical chain bromination of (+)-1-bromo-2-methylbutane yields (-)-1,2-dibromo-2-methylbutane of high optical purity. This observation requires a mechanism based on a bridged radical which is capable of maintaining its stereochemical configuration until reaction with molecular bromine occurs. Although thiyl radicals are just as capable of forming bridged radicals, similar evidence is not yet available. Conceivably, a similar bromination experiment to that of Skell's, but using (+)-1-methylthiyl-2-methylbutane, could give evidence of bridging for thiyl radicals.

One of the objectives of this thesis was to investigate the addition of thiyl radicals to a conjugated double bond and to a triple bond; it was hoped that for these systems the initial attack step would occur irreversibly, thus avoiding the kinetic complications previously described in this discussion.

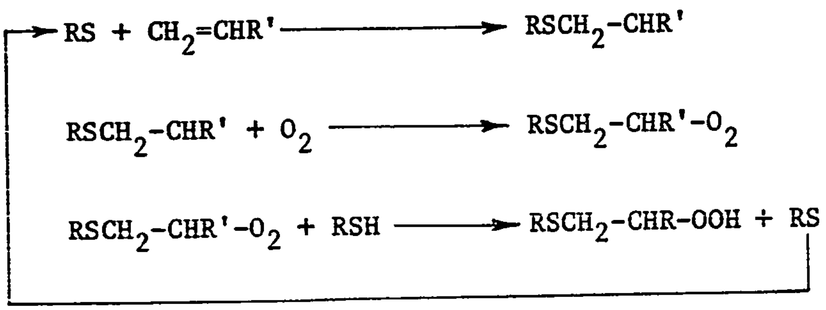
One of the ways of avoiding the reversibility of the thiyl attack step for mono-olefins is to introduce a radical scavenger which would react preferentially with the adduct radical and compete successfully with the reverse reaction. For this reason it was decided to investigate the co-oxidation of methanethiol and olefins in the gas phase.

Kharasch and co-workers were probably the first to be interested in co-oxidation (37): they obtained an 89 per cent yield of a 2-hydroxyethyl sulfoxide (R-SO-CH_2-CHR'-OH) when the free radical addition of n-propanethiol to styrene was carried out with an excess of dissolved oxygen. Kharasch suggested that the initial thiol-olefin co-oxidation products were hydroperoxides (R-S-CH_2-CHR'-OOH) which rearranged to give the observed hydroxysulfoxides.

Ford and co-workers (38) were able to substantiate Kharasch's hydroperoxide theory for co-oxidation when they obtained a 77 per cent hydroperoxide content during the co-oxidation of benzenethiol and indene. However the hydroperoxide product was not isolated due to the complete rearrangement to the hydroxysulfoxide within two hours.

More recently, Oswald and co-workers (39) have concluded that co-oxidation does proceed through the hydroperoxide intermediate by isolating these intermediates at 0°C for a variety of olefins and thiols. But no conclusions have been made about the rearrangement mechanism to the hydroxysulfoxide despite a continued interest in co-oxidation (40-41).

The free radical chain mechanism for the co-oxidation of thiols and olefins first postulated by Kharasch (37) was:



$$RS + CH_2{=}CHR' \longrightarrow RSCH_2\text{-}CHR'$$

$$RSCH_2\text{-}CHR' + O_2 \longrightarrow RSCH_2\text{-}CHR'\text{-}O_2$$

$$RSCH_2\text{-}CHR'\text{-}O_2 + RSH \longrightarrow RSCH_2\text{-}CHR\text{-}OOH + RS$$

This mechanism is consistent with the thermochemistry of co-oxidation which may be discussed by making use of a recent compilation of thermodynamic data on peroxy radicals and hydroperoxides, mostly on the part of Benson (45). The formation of a peroxy radical during co-oxidation,

$$RS\text{-}CH_2\text{-}CHR' + O_2 \longrightarrow RS\text{-}CH_2CHR'\text{-}OO,$$

has been estimated to be exothermic by about 28 kcal from the bond strength, $D(R\text{-}O_2)$, of alkyl peroxy radicals. This means that energy-rich peroxy radicals, RO_2^*, are formed but these should be deactivated at nearly every collision. The formation of a hydroperoxide, as the next step during co-oxidation,

$$RS\text{-}CH_2\text{-}CHR'\text{-}OO + RS\text{-}H \longrightarrow RS + RS\text{-}CH_2\text{-}CHR'\text{-}OOH,$$

is not expected to be very exothermic because the S-H bond strength of thiol, $D(RS\text{-}H) = 90$ kcal, is almost equal to the hydroperoxide bond strength, $D(RO_2\text{-}H) = 90 \pm 2$ kcal. At the present time, no rate constants are available for the abstraction of hydrogen atoms from either thiol or hydrogen bromide by peroxy radicals but in general, hydrogen bromide is expected to react faster since $D(H\text{-}Br)$ is only 87 kcal.

Hurst, Skirrow, and Tipper (46) have already carried out a kinetic investigation of the co-oxidation of hydrogen bromide with isobutene in the gas phase between 100 and 200°C. The reaction was followed by observing the decrease in pressure at constant volume, the main products being $Br\text{-}CH_2\text{-}C(CH_3)_2\text{-}OOH$ and a diperoxide. Due to autocatalysis it was impossible to obtain rate constants for the reaction but their results clearly indicate that the co-oxidation of HBr and isobutene is a chain process.

The work in this thesis is divided into three parts. The first part deals with the kinetics of the addition reaction while the second deals with the kinetics of the co-oxidation reaction. The last part is concerned with developing a general method for determining relative reactivities of olefins toward thiyl radicals. Some of the factors which determine relative reactivities are discussed as well.

EXPERIMENTAL

1. Materials

All of the hydrocarbons used were handled in a conventional vacuum manifold and purified by successive trap-to-trap distillations at 10^{-6} torr before being introduced into the storage bulbs. At least one more distillation was carried out before the preparation of a blend. If the blended gases were stored for long periods, they were again degassed before use. When additional purification by gas chromatography was required, a 25 ft dimethylsulfolane column was used, and the desired fraction collected in a cold trap fitted with a Teflon stopcock.

Ethylene Phillips Petroleum Co. "Research Grade".
Purity determined as 99.9 mole per cent; the probable impurities being ethane and carbon dioxide.

Propylene Phillips Petroleum Co. "Pure Grade".
Purity rated as 99 mole per cent; the probable impurities being propane and carbon dioxide.

Cis-butene-2 Phillips Petroleum Co. "Pure Grade".
Purity rated as 99 mole per cent; the probable impurities being trans-butene-2, n-butane, and butene-1.

Trans-butene-2 Phillips Petroleum Co. "Pure Grade".
Purity rated as 99 mole per cent; the probable impurities being cis-butene-2, n-butane, butene-1, and butadiene-1,3.

Iso-butene Phillips Petroleum Co. "Pure Grade".

Purity rated as 99 mole per cent; the most probable impurities being iso-butane and butene-1.

n-Butane Phillips Petroleum Co. "Research Grade".

Purity rated as 99.99 mole per cent; the probable impurities being iso-butane and 2,2-dimethyl-propane.

Butadiene-1,3 Matheson Ltd. "Instrument Grade".

Purity rated as 99.5 per cent; the probable impurities being butene-1, n-butane, and some acetylenes.

Allene Matheson Ltd.

Purity rated as 97 per cent; the most probable impurities being propylene and methyl acetylene.

Acetylene Matheson Ltd. "Purified Grade".

Purity rated as 99.6 per cent; the most probable impurity being carbon dioxide. Acetylene was further purified by subliming it from bulb to bulb.

Methyl Acetylene Matheson Ltd.

Purity rated as 96 per cent; the most probable impurities being allene and propylene.

Oxygen Liquid Carbonic Ltd.

Purity rated as 99.5 per cent.

Methyl Mercaptan Eastman Kodak "Reagent Grade".

No impurities were found by gas chromatography.

2. Reaction Cell

Two cylindrical fused quartz reaction cells were used, one 2 cm in length and the other 10 cm, and both 5 cm in diameter with optically plane windows. The reaction cell was connected to the manifold by a greaseless Springham diaphragm valve. A differential recording manometer was attached to the cell by means of a 0.125 inch Kovar seal.

3. Temperature Regulation

The reaction cell was contained in a cylindrical aluminum block with quartz windows at both ends. A spiral groove around the cylinder was fitted with a copper cooling coil which could be connected to a regulated supply of cold nitrogen gas. Heating was obtained by using four calrod heating elements spaced equally through the length of the block. Temperature regulation was maintained by using an (Electronic Processes Corporation, 1300 Series) anticipating temperature controller which regulated the temperature to within ± 0.1°C.

4. Light Source and Filters

The light source used for all reactions was a Hanovia SH 616A high-pressure quartz mercury-vapour lamp operated at 1.2 amperes and 127 V D.C. using a Sorenson S. R. 100 Nobatron Ranger rectifier and voltage regulator. A system of three quartz lenses, 9 cm in diameter, was used to collimate the light beam. All the work was carried out with a solution filter of 2,7-dimethyl-3,6-diazocyclohepta-1,6-diene iodide. From the known spectral energy distribution of the lamp (22) and the transmission characteristics of the filter (22), the initiation could be attributed to three lines at 2537, 2571, and 2652 A.

The order dependence on initiation was obtained by using neutral density filters which consisted of fine wire screens with measured transmissions of 18.0, 26.6, and 40.5 per cent, respectively. This filter was placed in the collimated beam of light, immediately before the cell.

5. Pressure Measurements

Some of the reaction rates were obtained by following the pressure change in a static system at constant volume using a differential recording pressure gauge (Figure 1).

Basically, the operation of this gauge depended on the action of a stainless steel bellows (B) on the ferromagnetic core (C) of a linear variable differential transformer (D). A second matching bellows (A) was used as a temperature compensator for the first. The gauge was initially balanced by turning the core (C) along a threaded brass rod (E) until an electrical null was obtained. The cell, which was connected to the inside of bellows (B), was pressurized with reactants while an equalizing air pressure was applied externally to maintain an initial electrical null. An electrical output was then obtained from a displacement of the core (C) when a pressure change occurred in bellows (B).

The coil of the transformer (type 005 M-L, Schaevitz Engineering, Camden, New Jersey) was supplied by an audio oscillator (type 1311-A, General Radio, Concord, Massachusetts) operating at 2000 Hertz. A (type DM-2000-C, Schaevitz Engineering) demodulator was used to rectify and filter the a-c output of the transformer and the d-c output was measured on a 1 mv recorder.

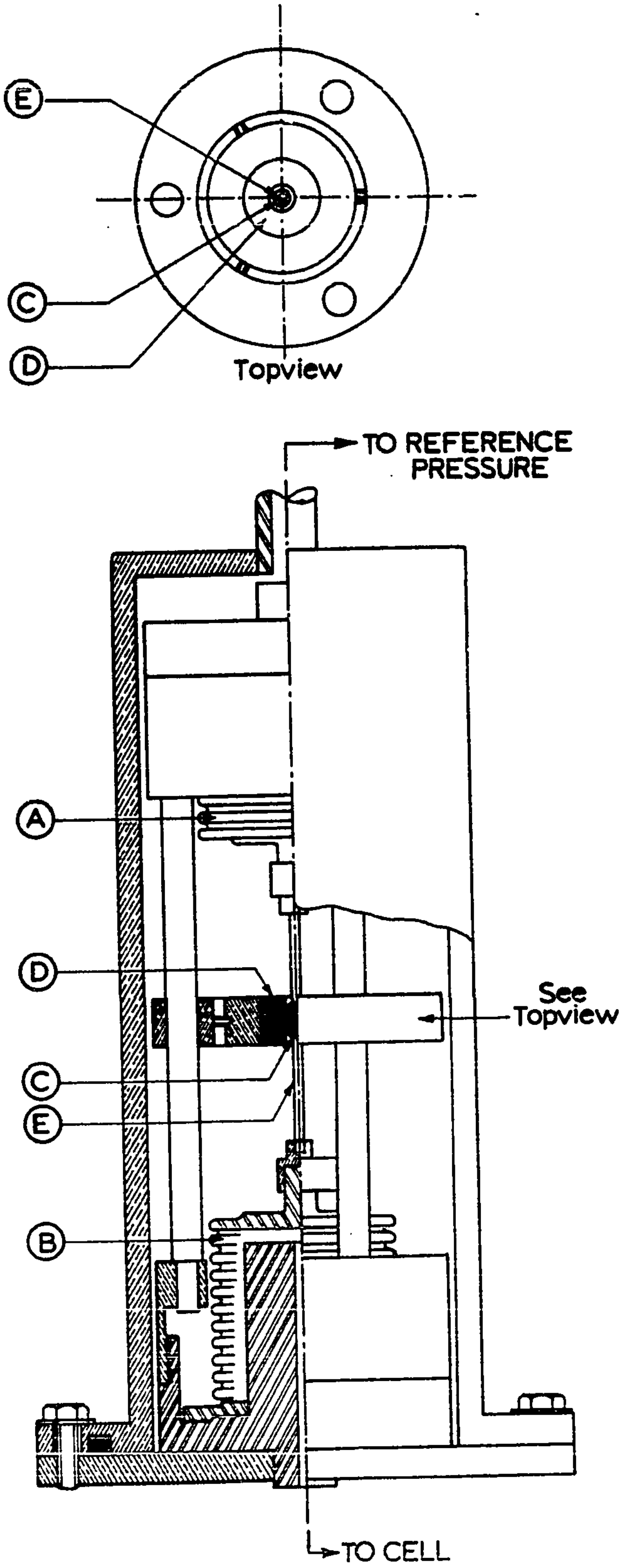


Fig.1 DIFFERENTIAL PRESSURE GAUGE

The electrical pressure gauge was calibrated against a McLeod gauge and normally operated with a 10 volt input and with an output sensitivity of 3 torr per millivolt. The pressure response was linear over a range of 0 to 50 torr. The internal dead volume of the gauge and connecting tubing was less than 1 per cent of the reaction cell and no correction was made for this volume.

6. Hydrocarbon Analysis

The analysis of hydrocarbons was carried out mainly by gas chromatography; a Perkin-Elmer, model 154, Vapour Fractometer (equipped with a flame ionization detector) was used. Initially a 300 ft propylene glycol capillary column was used, but improved separation was obtained on a 200 ft dimethylsulfolane column operating at 0°C. Additional product analyses were obtained by using a Consolidated mass spectrometer, model 21-620, which was modified with a specially constructed micro inlet system.

RESULTS AND DISCUSSION

I THE GENERAL MECHANISM

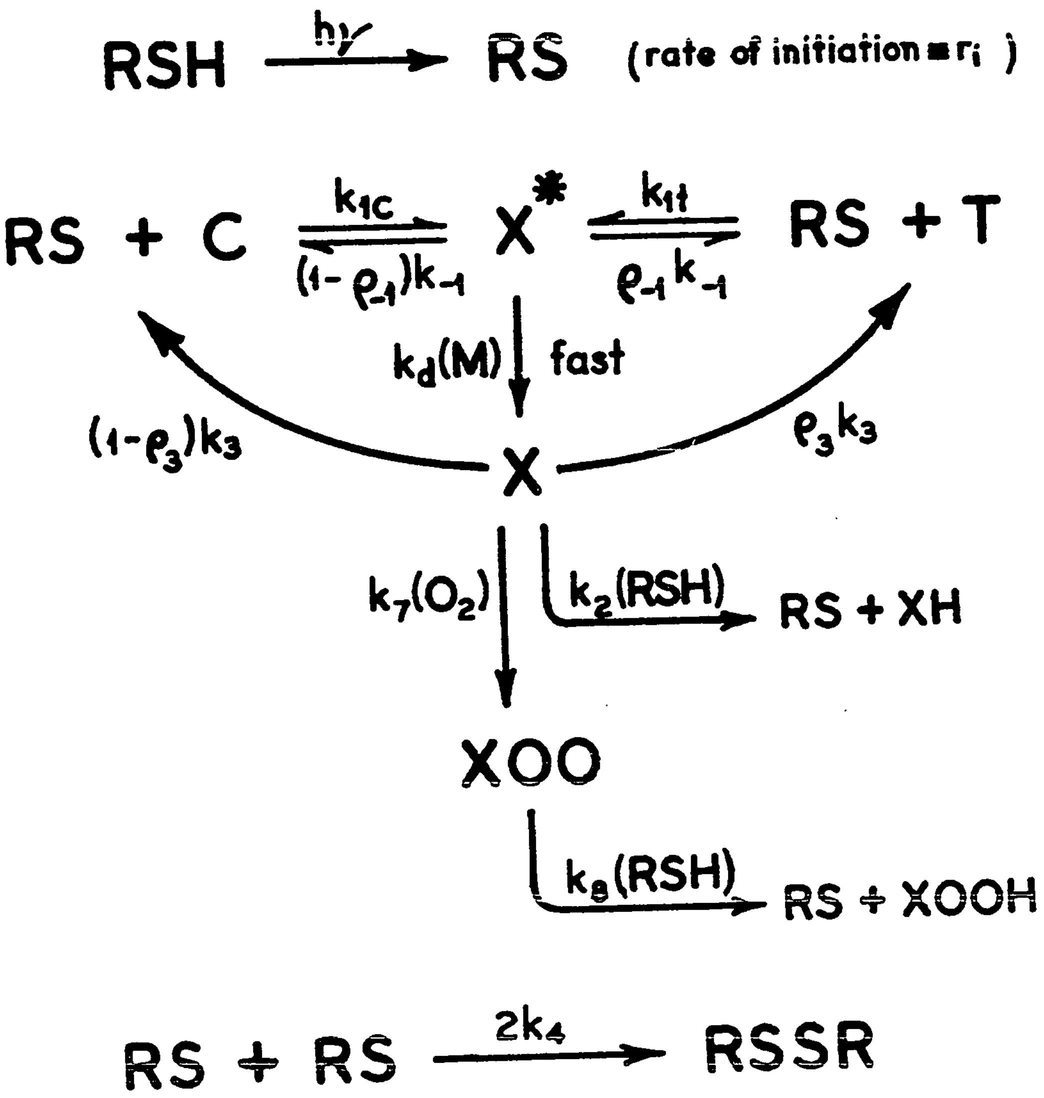
The free radical mechanism for the reaction of thiyl radicals with olefins in the gas phase as shown in Figure 2 will be used to explain the complete kinetics of isomerization, addition, and co-oxidation. The formation of an energized intermediate adduct radical, X^*, and the collisionally de-energized adduct radical, X, and a reverse reaction has been previously proposed (22-24) to explain the rapid isomerization of the unreacted olefin and the overall negative activation energy observed during the addition of methanethiol to olefins. The reversibility of the initial attack was found to be consistent with all the work presented in this thesis.

Similarly, the overall negative activation energy associated with co-oxidation has been attributed to the competition of the reverse reaction with the irreversible formation of a peroxy radical, XOO. The peroxy radical which subsequently abstracts hydrogen from a thiol group to form a hydroperoxide, XOOH, has been postulated as the main chain propagating species for gas phase co-oxidation.

The rate equations for isomerization, addition, and co-oxidation have been derived in Appendix 1 by the application of the steady-state approximation to the mechanism in Figure 2.

FIGURE 2

THE MECHANISM



C and T are the Cis and Trans form of the olefin

X^* and X are the energized and de-energized adduct radicals

ρ is the probability of decomposition to the Trans olefin

M is a colliding molecule that does not chemically react

RSH is thiol and RS is a thiyl radical

XOO is a peroxy radical and XOOH a hydroperoxide

1. Initiation

In order to obtain meaningful rate constants for free radical reactions, exact values are required for the rate of initiation and the rate of termination.

The rate of initiation has been obtained by previous workers (22, 23) from hydrogen evolution measurements from the photolysis of methanethiol in the absence of other reactants. In the following mechanism, hγ is a quantum of light responsible for photolysis:

$$CH_3SH + h\gamma \longrightarrow CH_3S + H$$

$$H + CH_3SH \longrightarrow CH_3S + H_2$$

Normally, the primary hydrogen atom abstracts a hydrogen atom from thiol, forming molecular hydrogen and a second thiyl radical. However, in the presence of olefin and oxygen, some hydrogen atoms probably react to form secondary radicals which eventually produce thiyl radicals by dehydrogenating thiol. Under these conditions, the overall reaction rate will not be seriously affected, provided that the chain length is sufficiently long.

A correction must be made for non-uniform illumination because the initiator absorbs light strongly. Appendix 3 contains the averaging procedure used to calculate the mean square root initiation, $(\overline{r_i^{\frac{1}{2}}})$, which was obtained by integrating the local rates of initiation over the cell length. All rate constant calculations in this thesis are based on averaged rates of initiation; the bar over the symbol is meant to denote this.

2. Termination

The dominant termination reaction may be uniquely determined from the reaction kinetics. In most cases to be discussed, termination was shown to occur by thiyl radical combination (reaction 4, Figure 2). The termination rate constant, k_4, has been determined (18,20) using the rotating sector technique and more recently (24,68) estimated as 2.5×10^9 liter mole^{-1} sec^{-1}.

In practice, for photo-initiated chain addition reactions, it is possible to determine the predominant termination process from the order dependence of the addition rate on the olefin concentration and initiation rate. According to the derivations given in Appendix 1, the following order dependencies should be observed with various terminations, where RS and X are defined in Figure 2:

Termination Reaction	Dependence on Initiation	Dependence on Olefin Concentration
RS + RS	Half Order	First Order
RS + X	Half Order	Half Order
X + X	Half Order	Zero Order
RS + wall	First Order	First Order
X + wall	First Order	Zero Order

Since the rate of initiation is proportional to the light intensity (see Appendix 3), the order dependence of the rate of addition on initiation was obtained by comparing rates of addition under two or more light intensities; calibrated wire mesh filters were used for this purpose.

II THE REACTION OF METHANETHIOL AND BUTADIENE-1,3

1. The Addition Reaction

(i) Mechanism: Recent kinetic investigations of the addition methanethiol to mono-olefins (22-24) have shown that thiyl attack constants on olefins cannot be obtained directly from rates of addition because of the reversibility of the initial attack. Only the rate constant ratio, k_1k_2/k_3, could be determined where the rate constants are those defined by Figure 2. However, it was demonstrated that attack constants for olefins may be determined from the kinetics of the cis-trans isomerization which occurs during the addition reaction. Obviously the isomerization method is limited to olefins which have cis and trans isomers, and consequently k_1 has been determined only for butene-2 and 1,2-ethylene-d_2.

The addition to butadiene, B, as will be shown later, is not reversible, due to the formation of a stable allylic adduct radical, Y. By analogy with the mono-olefin reaction, but for non-reversible addition, the mechanism under RS-RS termination is as follows, where r_i is the rate of initiation:

$$r_i \xrightarrow{\hspace{3em}} RS$$

$$RS + B \xrightarrow{k_{1b}} Y \qquad (1b)$$

$$Y + RSH \xrightarrow{k_2'} RS + \text{products} \qquad (2')$$

$$RS + RS \xrightarrow{k_4} RSSR \qquad (4)$$

Then applying the steady-state approximation to the reaction mechanism, the following relations are available by equating the rates of appearance to the rates of disappearance of the reaction intermediates, RS and Y:

$$r_i + k_2'[Y][RSH] = k_{1b}[RS][B] + 2k_4[RS]^2 \qquad (a)$$

$$k_{1b}[RS][B] = k_2'[Y][RSH] \qquad (b)$$

Summation of (a) and (b) leads to $[RS] = \left(\frac{r_i}{2k_4}\right)^{\frac{1}{2}}$.

Then by defining the initial rate of addition, R_a, as the initial rate of disappearance of butadiene,

$$R_a = \frac{-d[B]}{dt} = k_{1b}[RS][B] = \left(\frac{r_i}{2k_4}\right)^{\frac{1}{2}} k_{1b}[B] .$$

Therefore, under conditions which favour RS-RS termination, the thiyl attack constant for butadiene, k_{1b}, may be obtained directly from the rate of addition by using the derived rate equation. It was for this reason that the addition of CH_3SH to butadiene was investigated.

(ii) Rate of Addition: An attempt to obtain the attack constant for butadiene appeared to be complicated by heterogeneous wall effects, i.e. conditions favouring RS-RS termination were not obtained. The wall effect was first suspected when fogging of the reaction cell was observed during reaction.

From the variation of light intensity as shown in Table 1, the dependence of the rate of addition on initiation was shown to be first order, rather than the required half order dependence if RS-RS termination was to predominate.

TABLE 1

VARIATION OF LIGHT INTENSITY FOR BUTADIENE ADDITION AT 25°C

Filter Factor Per cent Transmission	$R_a \times 10^8$ no filter moles ℓ^{-1} sec^{-1}	$R_a \times 10^8$ with filter moles ℓ^{-1} sec^{-1}	Order Dependence on Initiation
40.5	2.99	1.21	1.01
26.6	3.20	0.88	0.98
18.0	3.43	0.62	1.00

$[B] = 1.61 \times 10^{-4}$ moles liter^{-1}

$[CH_3SH] = 0.86 \times 10^{-2}$ moles liter^{-1}

$(\overline{r_i^{1/2}})^2 = 6.04 \times 10^{-8}$ moles liter^{-1} sec^{-1}

Reaction Cell Length = 10 cm

From the results of Table 2 and 3, it is apparent that the rate of addition to butadiene is zero order with respect to both the butadiene and thiol concentration. This suggests the possibility that the reaction may have been occuring entirely on the walls of the reaction vessel; the observation of dense fogging of the cell surface during reaction would support this view.

Since initiation undoubtedly occurs homogeneously throughout the cell, it must be concluded that the addition to butadiene occurs in the gas phase as well, i.e. the reaction of thiyl radicals with butadiene is fast (as will be shown later). And since the reaction is practically independent of thiol, as indicated by the constant value of $R_a/(\overline{r_i^{1/2}})^2$ in Table 3, it must be concluded that the allylic adduct radicals, Y, are not dehydrogenating thiol effectively at 25°C, and

TABLE 2

ADDITION RATE DEPENCENCE ON BUTADIENE CONCENTRATION AT 25°C

Butadiene Concentration x 10^4 moles $liter^{-1}$	R_a Rate of Addition x 10^8 moles $liter^{-1}$ sec^{-1}
1.61	3.33
5.38	3.36
10.8	3.24
16.1	3.32

$[MeSH] = 1.08 \times 10^{-2}$ moles $liter^{-1}$

$\overline{(r_i^{\frac{1}{2}})}^2 = 6.64 \times 10^{-8}$ moles $liter^{-1}$ sec^{-1}

Reaction Cell Length = 10 cm

TABLE 3

DEPENDENCE OF ADDITION RATE ON THIOL CONCENTRATION AT 25°C

Methanethiol Concentration x 10^3 moles $liter^{-1}$	R_a Rate of Addition x 10^8 moles $liter^{-1}$ sec^{-1}	$\frac{R_a}{\overline{(r_i^{\frac{1}{2}})}^2}$
10.8	3.32	0.50
8.60	2.93	0.49
6.45	2.24	0.49
4.30	1.72	0.49

$[B] = 1.61 \times 10^{-3}$ moles $liter^{-1}$

Reaction Cell Length = 10 cm

hence participation in wall termination is probable. In fact, the chain lengths (the values of $R_a/(\overline{r_i^{\frac{1}{2}}})^2$ in Table 3) indicate that the rate of addition to butadiene depends only on the rate of initiation. Therefore, the addition to butadiene cannot be properly treated as a chain reaction.

In view of the fact that the desired addition kinetics were not obtained, it was concluded that the thiyl attack constant for butadiene, k_{1b}, could not be determined as planned. The only alternative was to obtain k_{1b} relative to another olefin. Since the reactivity of butene-2 has been determined from the isomerization kinetics (24), the next approach taken was to observe the effect of butadiene on the isomerization of butene-2. This approach proved successful and is described in section 2.

(iii) Products: The free radical addition of simple aliphatic thiols to butadiene-1,3 in solution has been known (47) to yield predominantly the 1,4-mono-adduct. More recent investigations (43) indicate that up to 5 per cent of the 1,2-mono-adduct is formed.

The findings of the present investigation, based on the mass spectrometric analysis of the heterogeneous methanethiol-butadiene addition products, indicate that the 1,4-mono-adduct is preferentially formed with up to 10 per cent of the 1,2-mono-adduct. Vapour phase chromatography indicates that approximately 5 per cent of the 1,2-mono-adduct and 1 per cent of higher molecular weight products are formed; the remaining product being the cis and trans 1,4-mono-adducts.

2. Inhibition of Cis-butene-2 Isomerization by Butadiene

Previous work (22,23) with cis-butene-2 and thiyl radicals in the gas phase at 25°C has shown that, for low thiol concentrations, the rate of isomerization is first order with respect to olefin and zero order with respect to thiol concentration when RS-RS termination predominates. The rate expression for the initial rate of isomerization, R_{ic}, which has been derived in Appendix 1 is as follows:

$$R_{ic} = -\left(\frac{d[C]}{dt}\right)_o = \left(\frac{r_i}{2k_4}\right)^{\frac{1}{2}} \rho_3 k_{1c}[C] .$$

(i) Isomerization Mechanism in the Presence of Butadiene:

The effect of trace quantities of butadiene, present as an impurity, was first observed (22) at high olefin concentrations when the rate of isomerization became independent of the olefin concentration. A simultaneous change in termination was also observed. This change in termination became apparent when the dependence on initiation changed from half to first order. These anomalous results did not occur after an estimated 0.002 mole per cent of butadiene was removed from the cis-butene-2 by gas chromatography.

The effect of adding known amounts of butadiene on the initial rate of isomerization of cis-butene-2 (shown in Table 4) indicates that a relatively small amount of butadiene has a substantial retarding effect. The constant value of R_{ic} x [B] in Table 4 indicates that the retarded rate of isomerization varies inversely with the butadiene concentration. Graph 1 also shows the inverse relation of the initial isomerization rate to the butadiene concentration.

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GRAPH 1

RELATION OF BUTADIENE TO THE RATE OF ISOMERIZATION

(C) = 5.38 x 10^{-1} moles liter^{-1}

(MeSH) = 2.15 x 10^{-1} moles liter^{-1}

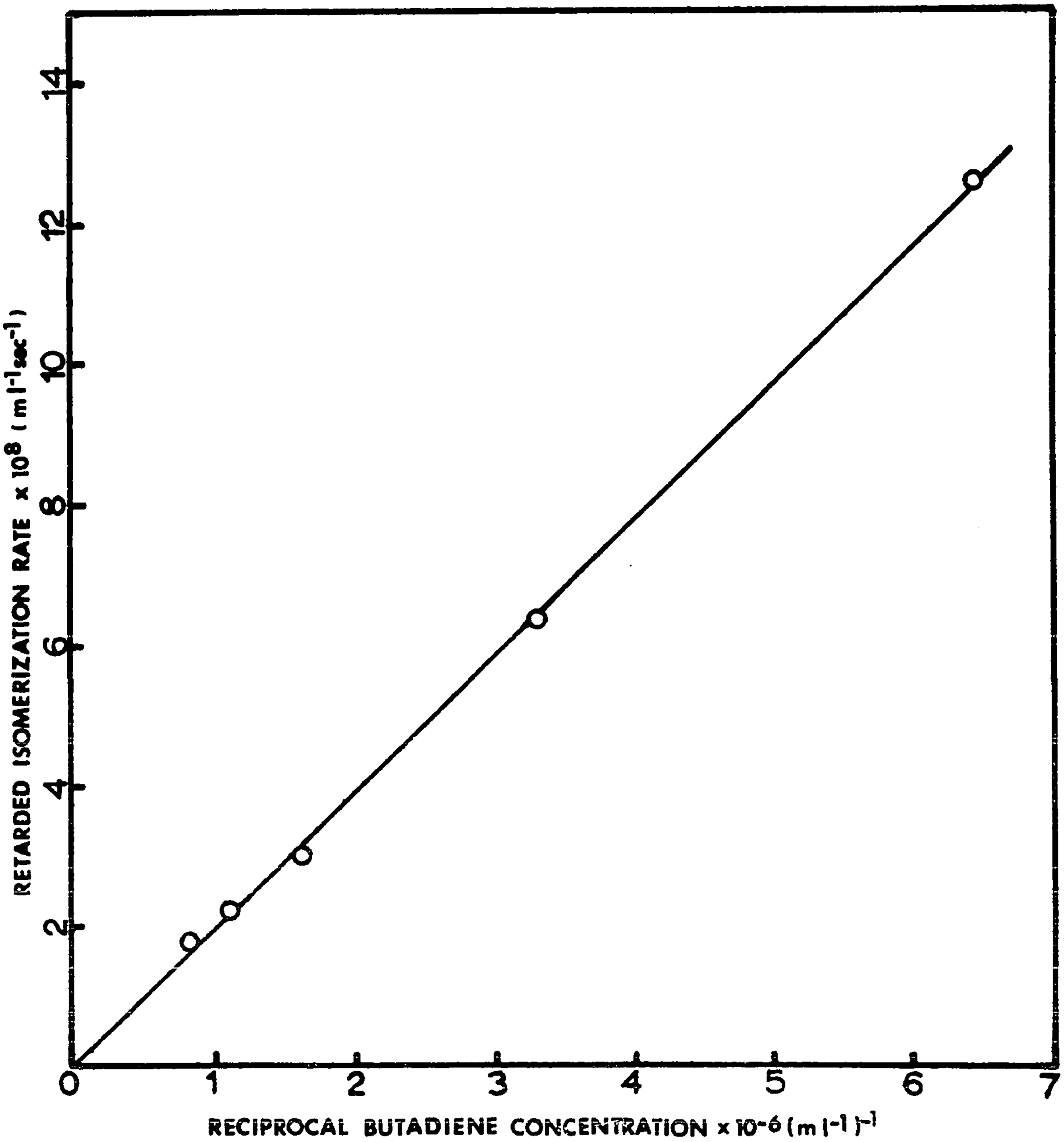


TABLE 4

EFFECT OF BUTADIENE-1,3 ON THE ISOMERIZATION RATE

Butadiene Concentration [B] moles $liter^{-1} \times 10^7$	Initial Rate of Isomerization $(R_{ic}) \times 10^8$ moles $liter^{-1}$ sec^{-1}	$(R_{ic}) \times [B]$ $\times 10^{14}$ $(moles\ liter^{-1})^2\ sec^{-1}$
0.00	25.9	——
1.56	12.6	1.96
3.04	6.36	1.94
6.19	2.98	1.84
9.14	2.20	2.01
12.2	1.79	2.17

$[C] = 5.38 \times 10^{-4}$ moles $liter^{-1}$

$[MeSH] = 2.15 \times 10^{-4}$ moles $liter^{-1}$

$(\overline{r_i^{1/2}})^2 = 4.60 \times 10^{-10}$ moles $liter^{-1}$ sec^{-1}

Temperature = 25°C

Reaction Cell Length = 10 cm

The isomerization in the presence of butadiene may be explained by the competitive reactions of butadiene and cis-butene-2 for thiyl radicals. Besides being a faster reaction, the addition of thiyl radicals to butadiene is not reversible at 25°C due to the formation of a stable allylic radical, Y. Benson (48) has determined the resonance energy of the methylallyl radical to be 12.6±1 kcal and therefore the activation energy for the decomposition of Y is at least 20 kcal (this estimation is based on the activation energy of about 10 kcal for the decomposition of a normal adduct radical plus the resonance energy).

The allylic radicals transfer with thiol relatively slowly, due to resonance stabilization, and the chain length for the addition to butadiene becomes short compared to the chain length for isomerization. Thus the irreversible removal of a small number of thiyl radicals by butadiene has a large effect on the rate of isomerization.

Harrison (11) has determined the transfer rate constant for the butanethiol-styrene system to be about 10^3 liter mole^{-1} sec^{-1}, which is considerably smaller than a value of 10^5 for the dehydrogenation of methanethiol by methyl radicals (66). This means that allylic radicals are not very effective dehydrogenating thiol, and hence, participation in termination is probable.

Therefore the following reactions may be used to explain the disappearance of butadiene:

$$\text{RS} + \text{B} \xrightarrow{k_{1b}} \text{Y}$$

$$\text{Y} + \text{RSH} \xrightarrow{k_2'} \text{RS} + \text{products}$$

$$\text{Y} \xrightarrow{k_w} \text{radical termination products}$$

(ii) Kinetics of Inhibition: The results of Table 5 show that the retarded rate of isomerization returns to the normal cis-trans isomerization rate after all the butadiene is exhausted and Graph 2 shows the resulting inhibition curves.

The inhibition period, t_i, may be used to measure the rate of disappearance of butadiene. The points of intersection of the extended straight portions of each plot in Graph 2 have been used to calculate the inhibition periods. This represents the time that would be required for all the butadiene to react if the initial mechanism continued to $[B] = 0$, and then changed abruptly to the uninhibited mechanism.

TABLE 5

PLOT OF BUTADIENE INHIBITION OF CIS-BUTENE-2 ISOMERIZATION (Graph 2)

2.07×10^{-7} moles liter^{-1}
Butadiene

Time (sec)	Isomerization (moles liter^{-1})
20	0.48×10^{-5}
40	1.05×10^{-5}
60	1.76×10^{-5}
80	3.15×10^{-5}
100	4.39×10^{-5}
120	5.72×10^{-5}

8.87×10^{-7} moles liter^{-1}
Butadiene

Time (sec)	Isomerization (moles liter^{-1})
60	0.49×10^{-5}
120	1.15×10^{-5}
160	2.12×10^{-5}
200	4.36×10^{-5}
220	5.87×10^{-5}

Absence of
Butadiene

Time (sec)	Isomerization (moles liter^{-1})
30	2.05×10^{-5}

15.5×10^{-7} moles liter^{-1}
Butadiene

Time (sec)	Isomerization (moles liter^{-1})
60	0.32×10^{-5}
100	0.51×10^{-5}
140	0.73×10^{-5}
180	1.12×10^{-5}
220	1.67×10^{-5}
260	2.65×10^{-5}
290	4.03×10^{-5}
300	4.53×10^{-5}
310	5.07×10^{-5}
320	5.73×10^{-5}

……

$[C] = 5.38 \times 10^{-4}$ moles liter^{-1}

$[MeSH] = 2.15 \times 10^{-4}$ moles liter^{-1}

Temperature = 25°C

Reaction Cell Length = 10 cm

$(\overline{r_i^{1/2}})^2 = 3.20 \times 10^{-9}$ moles liter^{-1} sec^{-1}

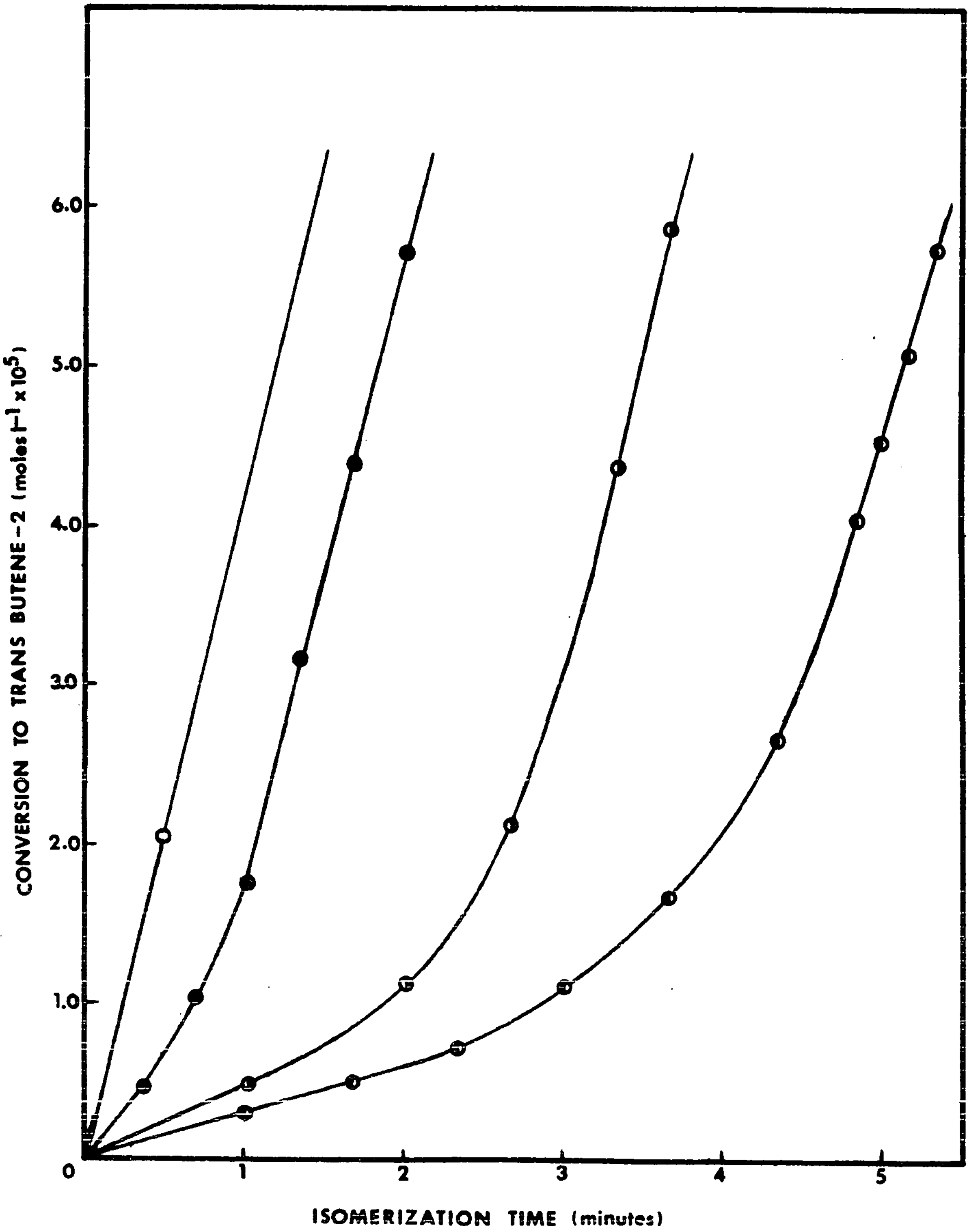
……

GRAPH 2

BUTADIENE INHIBITION OF CIS BUTENE-2 ISOMERIZATION

○ IN ABSENCE OF BUTADIENE   ◉ 8.874×10^{-7} m.l.$^{-1}$ BUTADIENE

● 2.071×10^{-7} m.l.$^{-1}$ BUTADIENE   ◉ 15.542×10^{-7} m.l.$^{-1}$ BUTADIENE



(iii) <u>Relative Reactivity of Butadiene</u>: A relationship based on the inhibition period, has been derived in Appendix 2, which gives the relative reactivity of cis-butene-2 and butadiene-1,3 towards thiyl radicals. The resulting expression,

$$R_{1c} = -\left(\frac{d[C]}{dt}\right)_o = \rho_3 \frac{k_{1c}}{k_{1b}} \frac{[C]_o}{t_i} ,$$

has been used to evaluate the relative attack constants, k_{1b}/k_{1c}, from the initial rate of isomerization, R_{1c}, and the corresponding inhibition period, t_i, (obtained from Graph 2) where k_{1c} and k_{1b} are the attack constants for cis-butene-2 and butadiene-1,3, respectively.

Table 6 contains the ratio of k_{1b}/k_{1c} for three butadiene concentrations. The average value obtained for k_{1b}/k_{1c} is 42.5ρx ρ_3, where ρ_3 is the probability factor that the trans olefin will be formed from the decomposition of X.

TABLE 6

RELATIVE REACTIVITY OF BUTADIENE

Butadiene Concentration $[B] \times 10^7$ moles liter^{-1}	Initial Rate of Isomerization $R_{1c} \times 10^8$ moles liter^{-1} sec^{-1}	Inhibition Period t_i sec	$\frac{k_{1b}}{k_{1c}}$
2.07	24.1	54	41.4 x ρ_3
8.87	8.16	152	43.4 x ρ_3
15.5	5.11	246	42.8 x ρ_3

$[C]_o = 5.38 \times 10^{-4}$ moles liter^{-1}

Temperature = 25°C

A value of 0.61 has been obtained for ρ_3 from work to be presented later in this thesis. Then using the experimental value of 42.5 x ρ_3 for k_{1b}/k_{1c}, butadiene-1,3 was found to be 25.9 times more reactive towards thiyl radicals than cis-butene-2.

From the isomerization kinetics of cis-butene-2 (23,68) $\rho_3 k_{1c}$ has been reported to be 1.6 x 10^6 liter $mole^{-1}$ sec^{-1} at 25°C and therefore the thiyl attack constant for butadiene-1,3 is 6.8 x 10^7 liter $mole^{-1}$ sec^{-1}.

The enhanced reactivity of butadiene over cis-butene-2 may be partly accounted for by the fact that there are two sites of attack on butadiene. Moreover, each site in butadiene probably receives less steric hinderance than in cis-butene-2, but steric factors undoubtedly are only minor factors to be considered when correlating relative reactivities of olefins towards thiyl radicals. For example, butene-2 is about four times more reactive towards thiyl radicals than ethylene (22); the steric factors introduced by alkyl substitution are overcome by simultaneous electron-donating inductive effects on the double bond. This increase in reactivity with substitution is consistent with the electrophilic nature of thiyl radicals. However, in the case of butadiene-1,3, particular attention must also be given to the fact that a resonance stabilized allylic radical is formed on addition which probably affects the rate by favouring the formation of a more stable intermediate radical.

(iv) Discussion of Method: The inhibition method which was developed in the present work is unique in several ways. For instance, the method does not depend on the rate of initiation which is normally a source of error. Also, the method does not depend on the ultimate fate of Y radicals which may either transfer with thiol or terminate. However, the method is contingent on the fact that addition occurs irreversibly or nearly so. In view of the resonance energy of 12 kcal of the Y radical, it is highly improbable that the addition to butadiene is reversible at 25°C, but until this is verified experimentally, the value of k_{1b} should be regarded as the lower limit.

Future experiments with butadiene should also include the temperature dependence of the inhibition period, since at low thiol concentrations such as those used in these experiments (2×10^{-4} mole liter^{-1}), the isomerization rate is independent of temperature (23), i.e. $E_a = 0.050 \pm 0.046$ kcal. Therefore, from the variation of the inhibition period with temperature, it should be possible to obtain the activation energy for the attack constant, k_{1b}. The present view is that thiyl radicals add to all olefins with essentially zero activation energy, but this question is not yet completely resolved.

This technique should be extended to include other conjugated diolefins such as 2,3-dimethyl-1,3-butadiene, isoprene, and chloroprene, which also yield predominantly the 1,4-mono-adduct with thiols (43), and possibly styrene, using cis-butene-2 as the standard reference; moreover, the feasibility of extending this technique to other radical systems, such as to the addition of Br or Cl atoms to olefins, should be investigated.

III THE REACTION OF METHANETHIOL AND ALLENE

The question of terminal vs. central attack for the addition thiols to allene (49,50) appears to have been successfully answered in favour of terminal attack. At room temperature, products thought to arise from terminal attack were favoured at 88 per cent over those from central attack; this increased to 95 per cent at -75°C.

However, the small portion of allylic radicals which result from central attack may complicate the addition kinetics to the extent that no rate constants may be determined.

1. Rate of Addition

Initial experiments with the methanethiol-allene system in the gas phase showed that methylacetylene was not formed at 25°C during the addition to allene. The slight fogging of the reaction cell surface indicated that wall effects were complicating the reaction.

Table 7 gives the effect of varying the light intensity for various allene concentrations which shows that the order dependence on initiation varies considerably. Above 5.38×10^{-4} moles liter^{-1} of allene wall termination completely predominates.

Table 7 also shows that the dependence on allene becomes zero order as the dependence on initiation approaches first order. The results of Table 7 are plotted in Graph 3 which shows that the rate of addition reaches a maximum at about 1.5×10^{-3} moles liter^{-1} of allene. Above this concentration the kinetics of addition to allene appear similar to the kinetics of addition to butadiene.

TABLE 7

VARIATION OF LIGHT INTENSITY FOR ALLENE ADDITION AT 25°C

Allene Concentration $\times 10^4$ moles ℓ^{-1}	$R_a \times 10^8$ no filter moles ℓ^{-1} sec^{-1}	$R_a \times 10^8$ 40.5% T filter moles ℓ^{-1} sec^{-1}	Order Dependence on Initiation
0.41	4.96	2.86	0.61
0.81	11.3	6.67	0.75
3.19	23.2	11.4	0.79
5.38	30.6	13.5	0.91
10.8	46.1	18.3	1.02
21.5	47.4	18.3	1.05
43.0	50.7	19.5	1.06

$[CH_3SH] = 8.61 \times 10^{-3}$ moles liter^{-1}

TABLE 8

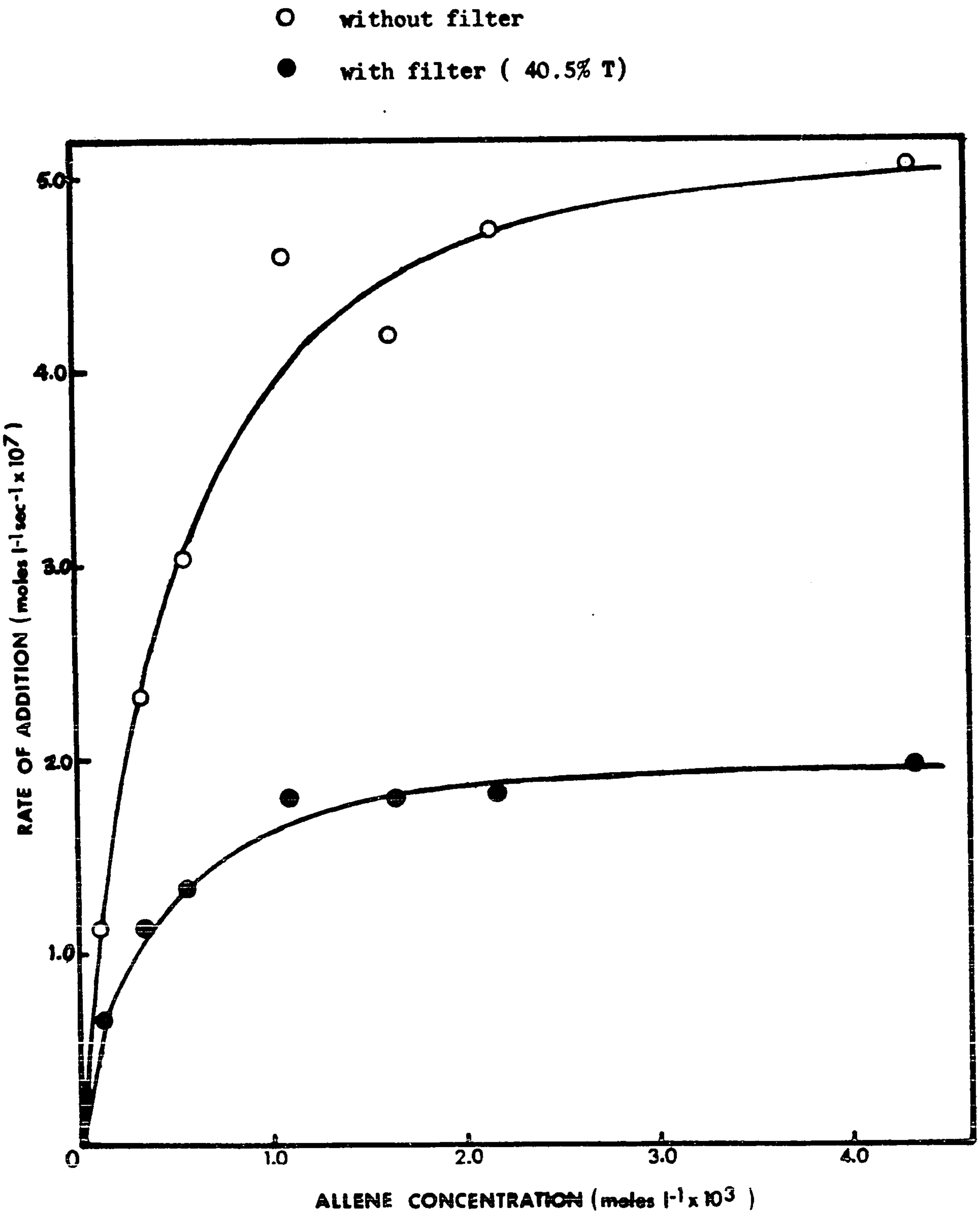
ALLENE ADDITION RATE DEPENDENCE AT LOW CONCENTRATIONS

Allene Concentration $\times 10^5$ moles liter^{-1}	R_a Rate of Addition $\times 10^8$ moles liter^{-1} sec^{-1}
1.97	1.21
2.98	1.96
4.13	2.49
6.13	3.80
8.25	5.39

$[MeSH] = 8.61 \times 10^{-3}$ moles liter^{-1}

GRAPH 3

DEPENDENCE OF ADDITION RATE ON ALLENE CONCENTRATION



2. The Addition Mechanism

At less than 5 x 10^{-3} moles liter^{-1} of allene, as shown in Table 8, the kinetics appear to be first order on allene. However, the lowest dependence on initiation was still 0.60, indicating some wall effects.

Due to heterogeneous wall effects, it was not possible to obtain rate constants directly from the addition kinetics. The relative reactivity of allene has been determined by the co-oxidation method which is to be discussed in section VI(6).

Unfortunately, the relative reactivity of allene cannot be obtained from the inhibition technique which was developed for conjugated olefins in section II(2), because terminal attack on allene is thought to occur reversibly.

IV THE REACTION OF METHANETHIOL AND ACETYLENE

The photo-chemically induced addition of methanethiol to acetylene in the gas phase has not been reported in the literature. An initial attempt by Andrews (15) in these laboratories has shown that the addition was rapid, indicating a chain reaction.

The addition of thiols to monosubstituted acetylenes (49-51) in the liquid phase has been shown to proceed in an anti-Markownikoff manner, which is the route giving the more stable intermediate radical.

In this study, the primary objective was to determine the reactivity of thiyl radicals with triple bonds. It was also necessary to establish whether the addition to a triple bond occurs reversibly.

The elucidation of the mechanism under RS-RS termination has shown that the adduct radical has a transfer rate comparable to its rate of unimolecular decomposition. Consequently, it was possible to obtain the attack constant for acetylene directly from the addition kinetics.

1. Kinetics of Addition

The rate expression for reversible addition under RS-RS termination which has been derived in Appendix 1, is as follows:

$$R_a = \frac{(r_i^{\frac{1}{2}})}{(2k_4)^{\frac{1}{2}}} \left[\frac{k_1[A]\ k_2[RSH]}{k_3 + k_2[RSH]} \right]$$

In the work to be presented it will be shown that the addition to acetylene follows this rate expression.

The results in Table 9 give the variation of the addition rate with the acetylene concentration, and Graph 4 shows that a first order dependence is obtained.

TABLE 9

ADDITION RATE DEPENDENCE ON ACETYLENE AT 25°C

Acetylene Concentration x 10^3 moles $liter^{-1}$	R_a Rate of addition x 10^7 moles $liter^{-1}$ sec^{-1}	Chain Length $\frac{R_a}{(\overline{r_i^{1/2}})^2}$
0.81	1.00	1.5
1.61	1.90	2.8
2.15	2.76	4.1
2.69	3.35	5.0
3.23	4.40	6.6

[MeSH] = 2.69×10^{-3} moles $liter^{-1}$

$(\overline{r_i^{1/2}})^2 = 6.71 \times 10^{-8}$ moles $liter^{-1}$ sec^{-1}

Cell Length = 2 cm (for all acetylene results)

The results of Table 10 for methylacetylene were obtained to see if the chain length for addition was affected by substitution. A comparison of Table 9 and Table 10 indicates that the chain length for the addition to methylacetylene is only slightly longer than that for acetylene under the same conditions. The increase in the chain length with substitution may be expected from an increase in reactivity of the triple bond, but a simultaneous decrease in the chain length may be expected from a decrease in the transfer rate (reaction 2, Figure 2) since the adduct radical obtained from methylacetylene is more stable.

GRAPH 4

DEPENDENCE OF ADDITION RATE ON ACETYLENE CONCENTRATION AT 25°C

(MeSH) = 2.69×10^{-3} moles liter^{-1}

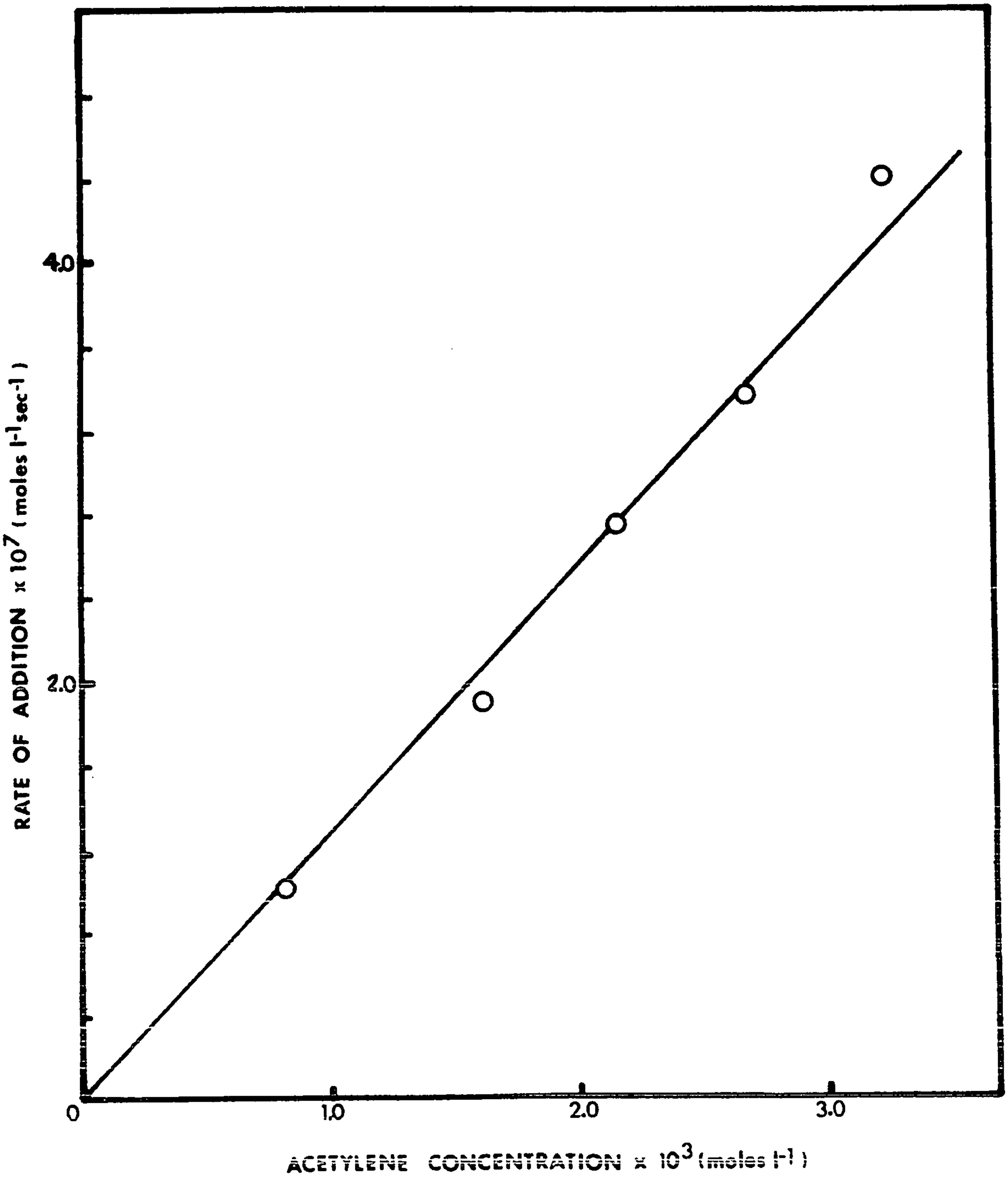


TABLE 10

ADDITION RATE DEPENDENCE ON METHYLACETYLENE AT 25°C

Methylacetylene Concentration $\times 10^3$ moles liter^{-1}	R_a Rate of Addition $\times 10^7$ moles liter^{-1} sec^{-1}	Chain Length $\frac{R_a}{\overline{(r_i^{1/2})}^2}$
0.27	1.05	1.6
0.54	2.20	3.3
1.08	3.59	5.4
1.61	3.73	5.6
2.15	5.29	7.8

$[\text{MeSH}] = 2.69 \times 10^{-3}$ moles liter^{-1}

$\overline{(r_i^{1/2})}^2 = 6.71 \times 10^{-8}$ moles liter^{-1} sec^{-1}

The variation of the addition rate with thiol concentration is given in Table 11 and Table 12 at different acetylene concentrations. The variation of $R_a/\overline{(r_i^{1/2})}$ with thiol indicates that the order dependence on thiol is complex.

However, the thiol dependence may be shown to follow the derived rate equation by using the reciprocal form of the equation,

$$\frac{\overline{(r_i^{1/2})}}{R_a} = (2k_4)^{1/2}\left[\frac{k_3}{k_1[A]\ k_2[RSH]} + \frac{1}{k_1[A]}\right],$$

which is in the form of a straight line at constant acetylene concentration when $\overline{(r_i^{1/2})}/R_a$ is plotted against the reciprocal thiol concentration. Graph 5, based on Table 11 and Table 12, shows that this form of the equation results in a linear plot.

TABLE 11

ADDITION RATE DEPENDENCE ON THIOL CONCENTRATION AT 25°C

Methanethiol Concentration x 10^3 moles liter^{-1}	R_a Rate of Addition x 10^7 moles liter^{-1} sec^{-1}	$\frac{R_a}{(\overline{r_i^{1/2}})}$ x 10^3	$\frac{R_a}{(\overline{r_i^{1/2}})^2}$
2.15	2.44	0.96	3.8
2.69	3.07	1.04	3.6
3.23	3.82	1.19	3.7
3.77	4.36	1.25	3.6
4.30	5.04	1.38	3.8
4.84	5.35	1.39	3.6
5.96	6.51	1.57	3.8
9.14	8.48	1.80	3.8

[Acetylene] = 2.15 x 10^{-3} moles liter^{-1}

TABLE 12

ADDITION RATE DEPENDENCE ON THIOL CONCENTRATION AT 25°C

Methanethiol Concentration x 10^3 moles liter^{-1}	R_a Rate of Addition x 10^7 moles liter^{-1} sec^{-1}	$\frac{R_a}{(\overline{r_i^{1/2}})}$ x 10^4	$\frac{R_a}{(\overline{r_i^{1/2}})^2}$
2.15	1.33	5.24	2.0
2.69	1.60	5.44	1.9
3.50	1.95	5.80	1.7
4.30	2.54	6.94	1.9
5.92	3.38	8.16	2.0
7.53	3.74	8.50	1.9
9.14	4.18	8.89	1.9
10.8	4.84	9.96	2.0

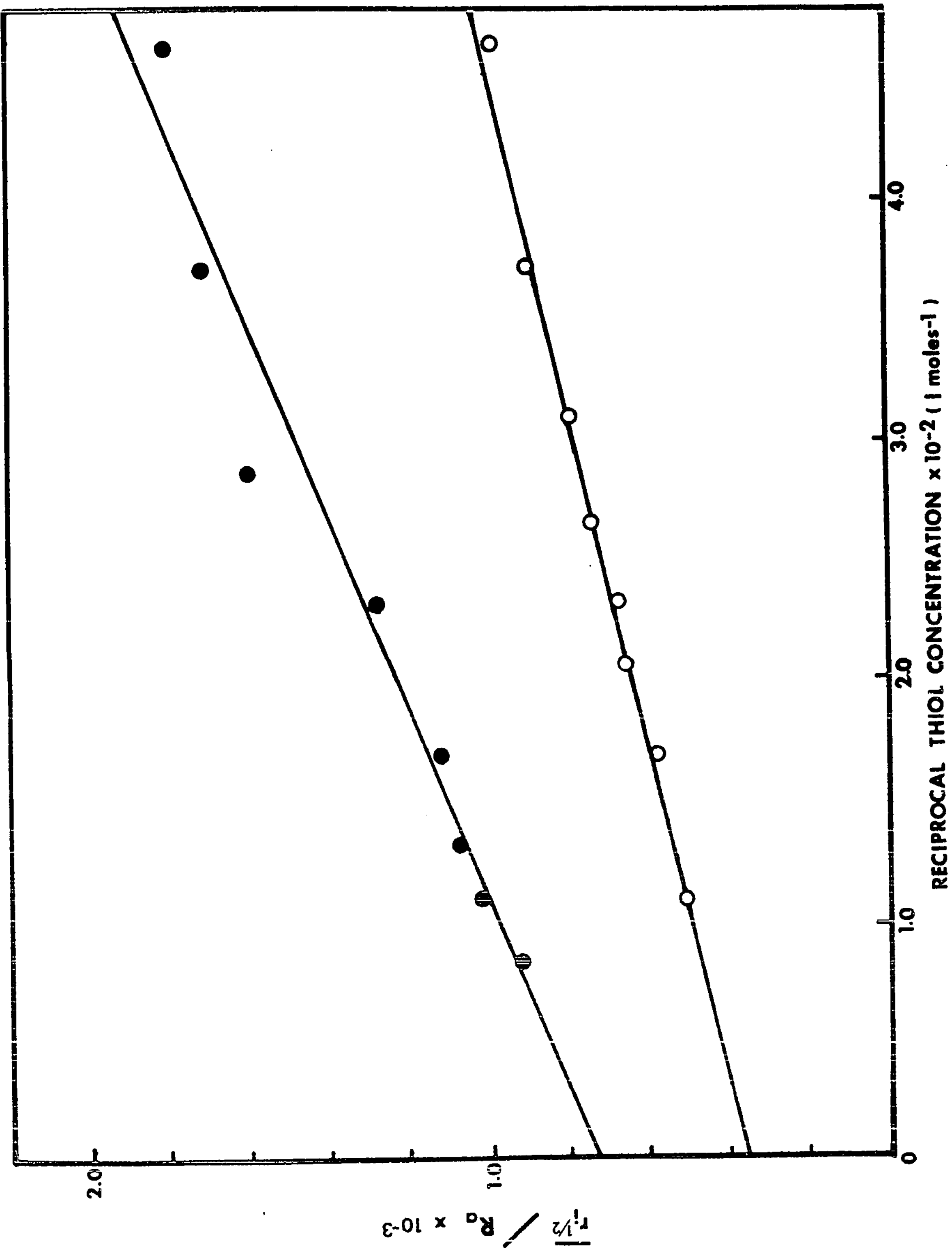
[Acetylene] = 1.08 x 10^{-3} moles liter^{-1}

GRAPH 5

DEPENDENCE OF ADDITION RATE ON THIOL CONCENTRATION AT 25°C

● (Acetylene) = 1.08×10^{-3} moles liter^{-1}

○ (Acetylene) = 2.15×10^{-3} moles liter^{-1}



2. Calculation of Rate Constants

From the plot of the reciprocal rate equation for acetylene, it is possible to obtain k_1 from the intercept since k_4 is known, and k_2/k_3 from the ratio of the slope to the intercept.

A least squares treatment has been applied to the linear plots of Graph 5. The values obtained for k_1 were 8.00×10^4 and 7.86×10^4 liter mole^{-1} sec^{-1} (7.93×10^4 averaged) and the corresponding values for k_2/k_3 were 297 and 270 liter mole^{-1} (284 averaged).

3. Temperature Dependence of Addition

Table 13 indicates an overall negative activation energy for addition to acetylene which varies from -2.2 kcal at 9.15×10^{-3} moles liter^{-1} of thiol, to -3.9 kcal at 2.15×10^{-3} moles liter^{-1} of thiol. It is apparent from these results that the attack step is reversible since the rate decreases with increasing temperature.

TABLE 13

EFFECT OF TEMPERATURE ON THE RATE OF ADDITION TO ACETYLENE

Thiol Concentration x 10^3 moles liter^{-1}	$(\overline{r_i^{1/2}})$ x 10^4 (moles liter^{-1} sec^{-1})$^{1/2}$	R_a (moles liter^{-1} sec^{-1}) x 10^7			
		25°C	40°C	55°C	70°C
2.15	3.36	3.24	2.32	1.72	1.37
2.69	4.00	4.40	3.28	2.36	1.85
3.77	5.00	6.62	5.58	3.58	2.78
5.38	6.18	9.54	8.94	5.66	4.72
9.14	8.90	15.3	14.6	10.9	9.78

$[A] = 2.02 \times 10^{-3}$ moles liter^{-1}

The temperature dependence of the rate constant ratio, k_2/k_3, for acetylene has been obtained from the least square treatment of the data in Table 13 which has been shown to follow the reciprocal rate expression in Graph 6. Table 14 gives k_2/k_3 at various temperatures.

TABLE 14

EFFECT OF TEMPERATURE ON k_2/k_3 FOR ACETYLENE

Temperature °K	$1/T \times 10^3$	k_2/k_3 liter mole^{-1}	log (k_2/k_3)
298.2	3.353	294	2,468
313.2	3.193	194	2.288
328.2	3.046	118	2.072
343.2	2.914	87.4	1.942

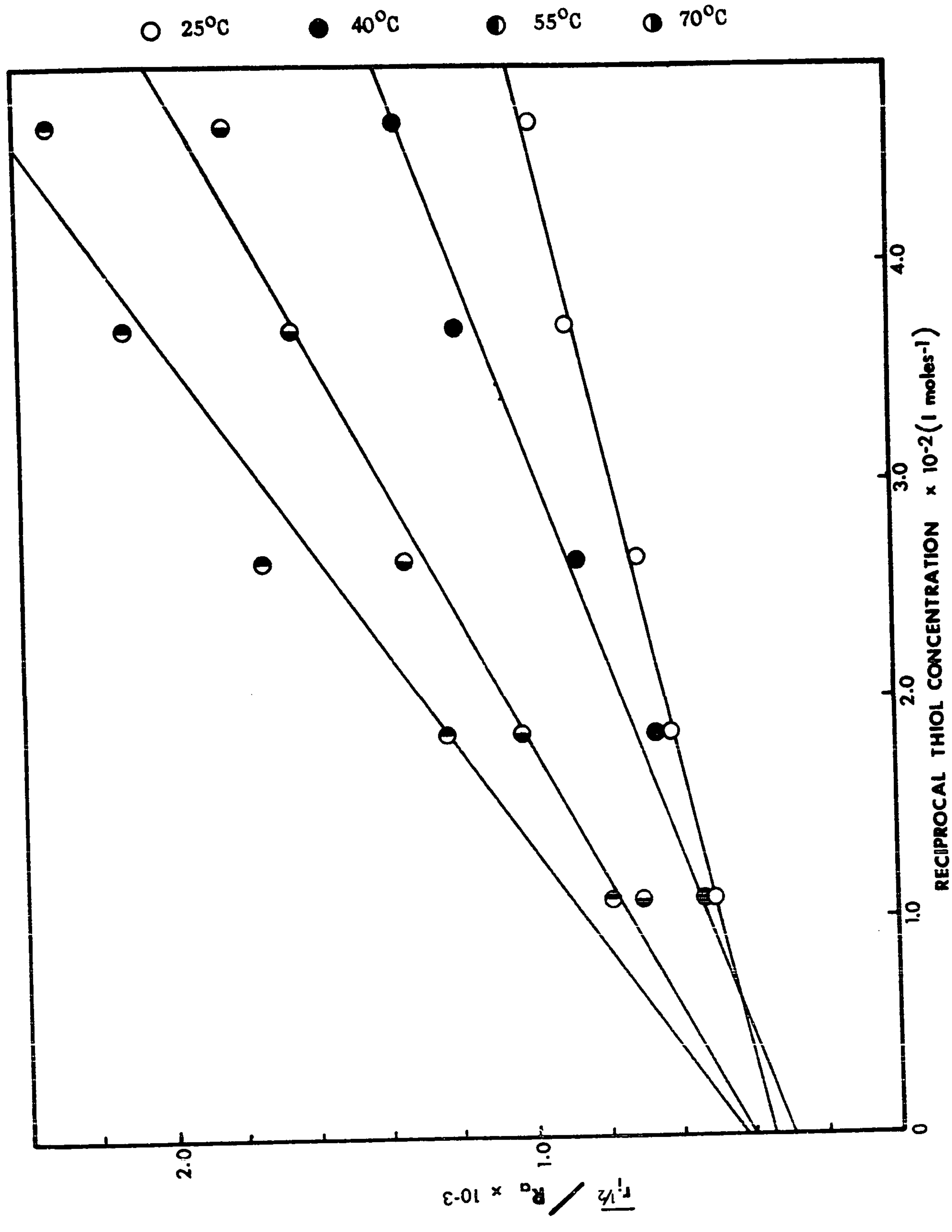
The activation energy for the ratio k_2/k_3 has been evaluated by the least squares treatment of the data in Table 14. A value of -5.6 kcal was obtained for E_2-E_3, and the corresponding Arrhenius plot is shown in Graph 7.

Similar activation energies have been obtained for the photobromination of acetylene (52,53), which also occurs reversibly with $(E_2-E_3) = -5.8$ kcal, but wall termination of Br atoms greatly complicated the kinetics.

Graph 6 contains the reciprocal plot for acetylene at various temperatures. The variation of the intercept in Graph 6 indicates that E_1 is probably close to zero (the intercepts are those obtained by the method of least squares).

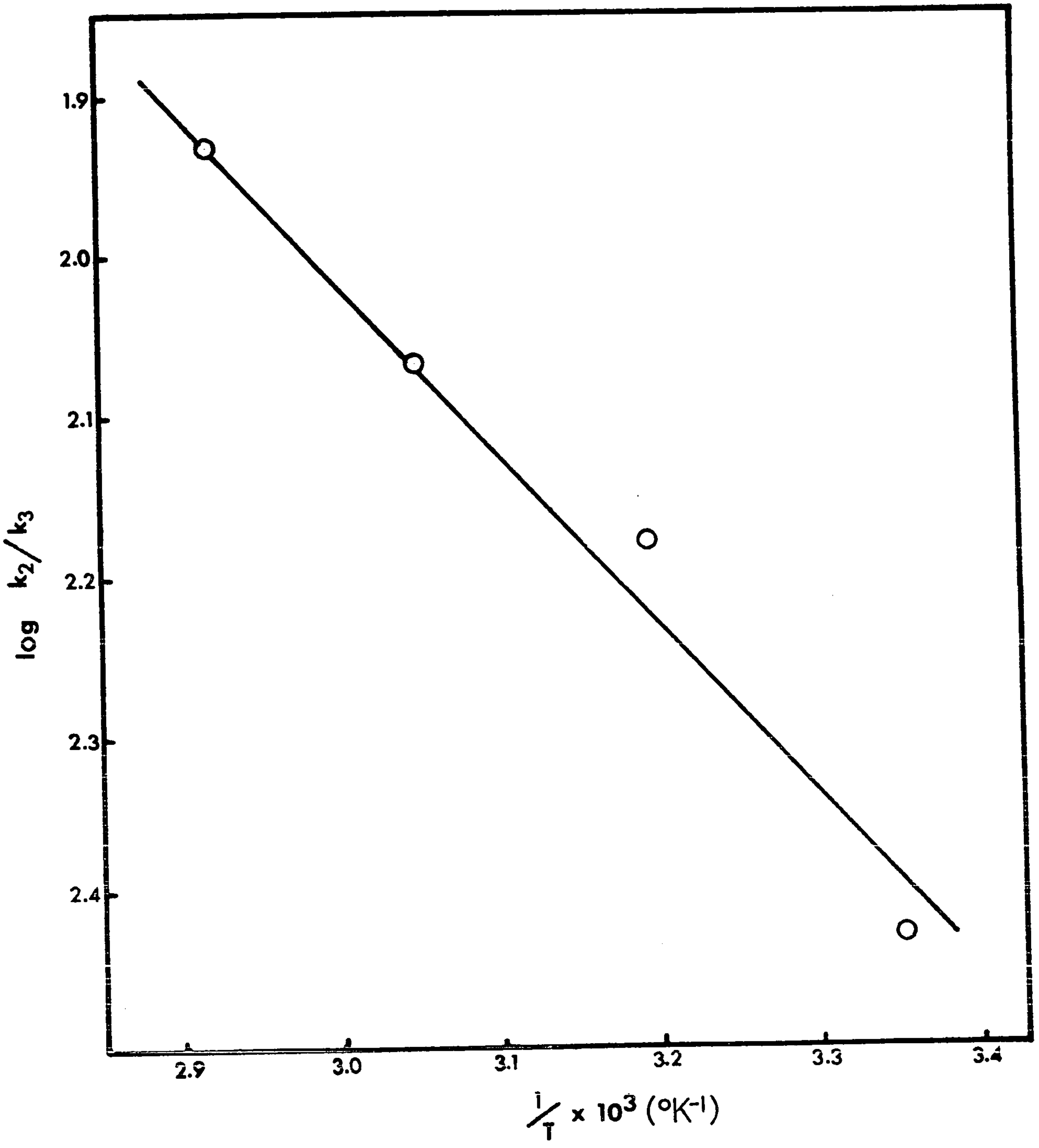
GRAPH 6

TEMPERATURE DEPENDENCE OF ADDITION TO ACETYLENE



GRAPH 7

ARRHENIUS PLOT OF k_2/k_3 FOR ACETYLENE



4. Comparison of Rate Constants

A comparison of attack constants for acetylene ($k_1 = 7.9 \times 10^4$ liter mole^{-1} sec^{-1}, this work at 25°C) and ethylene ($k_1 = 4.8 \times 10^5$ liter mole^{-1} sec^{-1}, other work (23) at 25°C), indicates that ethylene is 6.1 times more reactive towards thiyl radicals. In similar comparisons, ethylene was found 3.6 times more reactive than acetylene towards CF_3 radicals (54), while CH_3 radicals (55) were only 1.3 times more reactive towards ethylene than acetylene. Since the addition to acetylene and ethylene probably occur with minimal steric hindrance, these comparisons serve to illustrate the electrophilic tendencies of CH_3S and CF_3 radicals while CH_3 is clearly nucleophilic.

A comparison of k_2/k_3 values for several olefins (24) is contained in Table 15 along with the corresponding E_2-E_3 values (based on $E_1+E_2-E_3$, assuming $E_1=0$) which have been determined in Appendix 4.

TABLE 15

COMPARISON OF k_2/k_3 FOR SEVERAL OLEFINS AT 25°C

Olefin	k_2/k_3 (liter mole^{-1})	E_2-E_3 (kcal)
2-Butene	0.76	-6.4
Ethylene	4.1	-5.0
Acetylene	284	-5.6

Unfortunately present studies have not been able to separate the rate constants, k_2 and k_3, but from the much higher k_2/k_3 ratio for acetylene, one can only surmise that the vinylic adduct radicals, which are obtained from the addition to acetylene, are very effective in dehydrogenating thiol, as compared to the alkyl adduct radicals obtained from ethylene, assuming similar values of k_3 for acetylene and ethylene.

Although little is known about the reactivity of vinyl radicals, it has been suggested that they are very reactive and that they are responsible for the mercury-photosensitized polymerization of acetylene (59-61). But more consistent with the reactivity observed in this study, vinyl radicals (62), formed by the photolysis of mercury divinyl at 50°C in the gas phase, are known to readily abstract hydrogen from isobutane.

Some of the factors which determine the relative reactivity of various olefins (including acetylene) towards thiyl radicals are discussed in section VI(3).

V THE CO-OXIDATION REACTION

The kinetics of the gas phase co-oxidation of methanethiol with olefins was investigated primarily to develop a method for determining the reactivity of olefins towards thiyl radicals. The free radical mechanism for co-oxidation as shown in Figure 2 is closely related to the normal addition reaction. During the co-oxidation reaction, the adduct radical which normally dehydrogenates thiol, reacts irreversibly with oxygen to from a peroxy radical, XOO. The peroxy radical then dehydrogenates thiol to form a hydroperoxide and a thiyl radical. Therefore, co-oxidation is a chain process.

1. Isomerization in the Presence of Oxygen

Previous work in the gas phase by Andrews (18) has shown that small quantities of oxygen inhibit the addition of methanethiol to propylene at 25°C. This observation was confirmed by Pallen (20) who showed that oxygen also retards the isomerization of butene-2. Both effects were attributed to the co-oxidation process. The reaction of oxygen with the adduct radical should be very fast since the rate constant at 22°C for the reaction of ethyl radicals with oxygen is 4.2×10^9 liter mole^{-1} sec^{-1} (63).

The approach used initially in this investigation was to observe the effect of small quantities of oxygen on the isomerization of cis-butene-2 as shown in Table 16.

TABLE 16

EFFECT OF OXYGEN ON THE ISOMERIZATION RATE AT 25°C

Oxygen Concentration $\times 10^5$ moles liter^{-1}	Initial Rate of Isomerization $(R_{ic}) \times 10^7$ moles liter^{-1} sec^{-1}
0.00	6.37
0.51	4.33
1.02	2.83
2.04	1.96
3.07	1.52

$[C] = 5.38 \times 10^{-4}$ moles liter^{-1}

$[RSH] = 2.15 \times 10^{-4}$ moles liter^{-1}

Cell Length = 10 cm.

$\left(\overline{r_i^{1/2}}\right)^2 = 2.77 \times 10^{-9}$ moles liter^{-1} sec^{-1}

The results in Table 16 show that the rate of isomerization at 25°C is markedly reduced by a factor of about one half by the introduction of less than 0.2 torr oxygen (10^{-5} mole liter^{-1}).

The dependence of the rate on oxygen concentration was found to follow a simple rate expression for isomerization in the presence of oxygen which has been derived in Appendix 1.

$$R_{ic} = -\left(\frac{d[C]}{dt}\right)_o = \frac{\overline{(r_i^{1/2})}}{(2k_4)^{1/2}}\left[\frac{\rho_3 k_{1c} k_3 [C]}{k_3 + k_7[O_2]}\right],$$

where the rate constants are those defined in Figure 2. It has been assumed that RS-RS termination continues to predominate at small oxygen concentrations.

By using the reciprocal form of the isomerization rate expression, $1/R_{ic}$ = (constant)$k_7/k_3[O_2]$ + (constant), a linear plot was obtained (see Graph 8) when $1/R_{ic}$ was plotted against the oxygen concentration. From the ratio of the slope to the intercept of this plot, a value of 1.1×10^5 liter $mole^{-1}$ was obtained for the rate constant ratio, k_7/k_3.

Table 17a gives the effect of oxygen on the rate of isomerization of cis-butene-2 at various temperatures (a different initiation rate was used than for the results in Table 16); the reciprocal plots are shown in Graph 9 and the corresponding k_7/k_3 values are listed in Table 17b. The Arrhenius plot for k_7/k_3 is shown in Graph 10 which gives a value of 7.1 kcal for the activation energy difference E_3-E_7.

TABLE 17a

EFFECT OF OXYGEN ON ISOMERIZATION AT VARIOUS TEMPERATURES

Oxygen Pressure (torr)	$(R_{ic}) \times 10^8$ (moles $liter^{-1}$ sec^{-1}) -20°C	25°C	100°C
0.00	22.4	25.7	24.8
0.18	1.14	10.8	22.1
0.36	0.53	5.99	20.7
0.54	____	4.32	20.1

$[C] = 5.38 \times 10^{-4}$ moles $liter^{-1}$

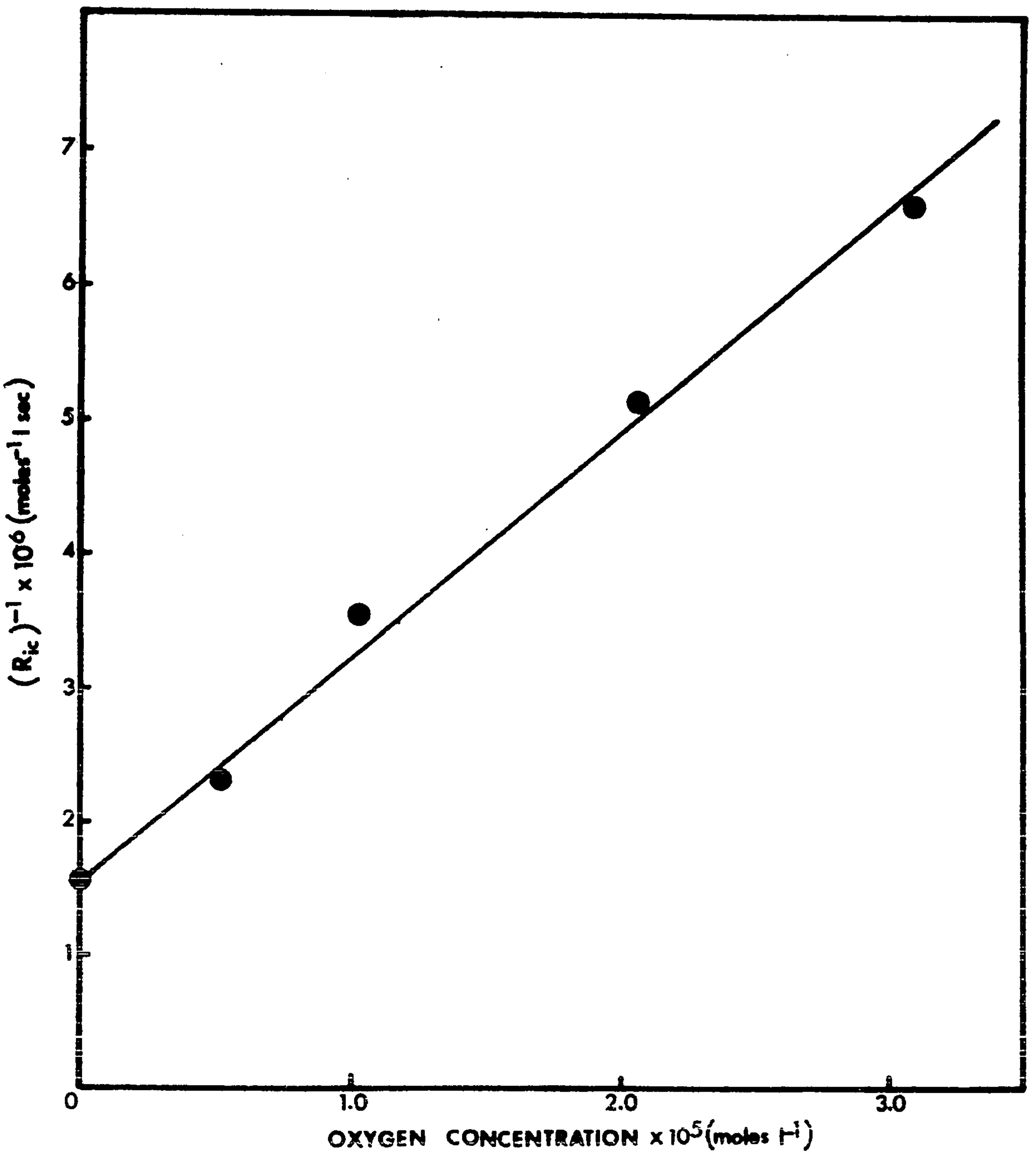
$[RSH] = 2.15 \times 10^{-4}$ moles $liter^{-1}$

Cell Length = 10 cm.

$\overline{(r_i^{\frac{1}{2}})^2} = 4.0 \times 10^{-10}$ moles $liter^{-1}$ sec^{-1}

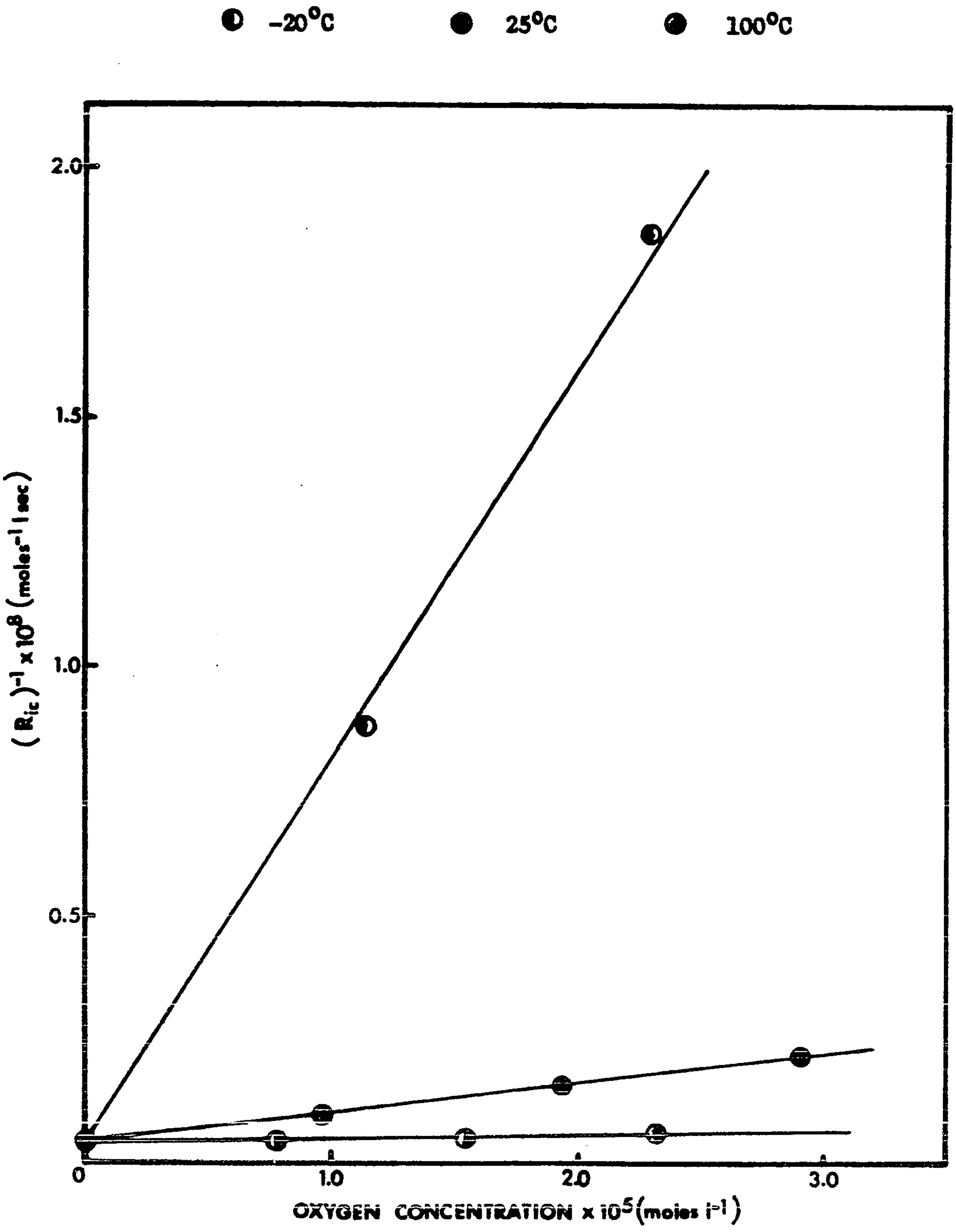
GRAPH 8

EFFECT OF OXYGEN ON ISOMERIZATION AT 25°C



GRAPH 9

EFFECT OF OXYGEN ON ISOMERIZATION AT VARIOUS TEMPERATURES



GRAPH 10

ARRHENIUS PLOT OF k_7/k_3 FROM CIS-BUTENE-2 ISOMERIZATION IN THE PRESENCE OF OXYGEN

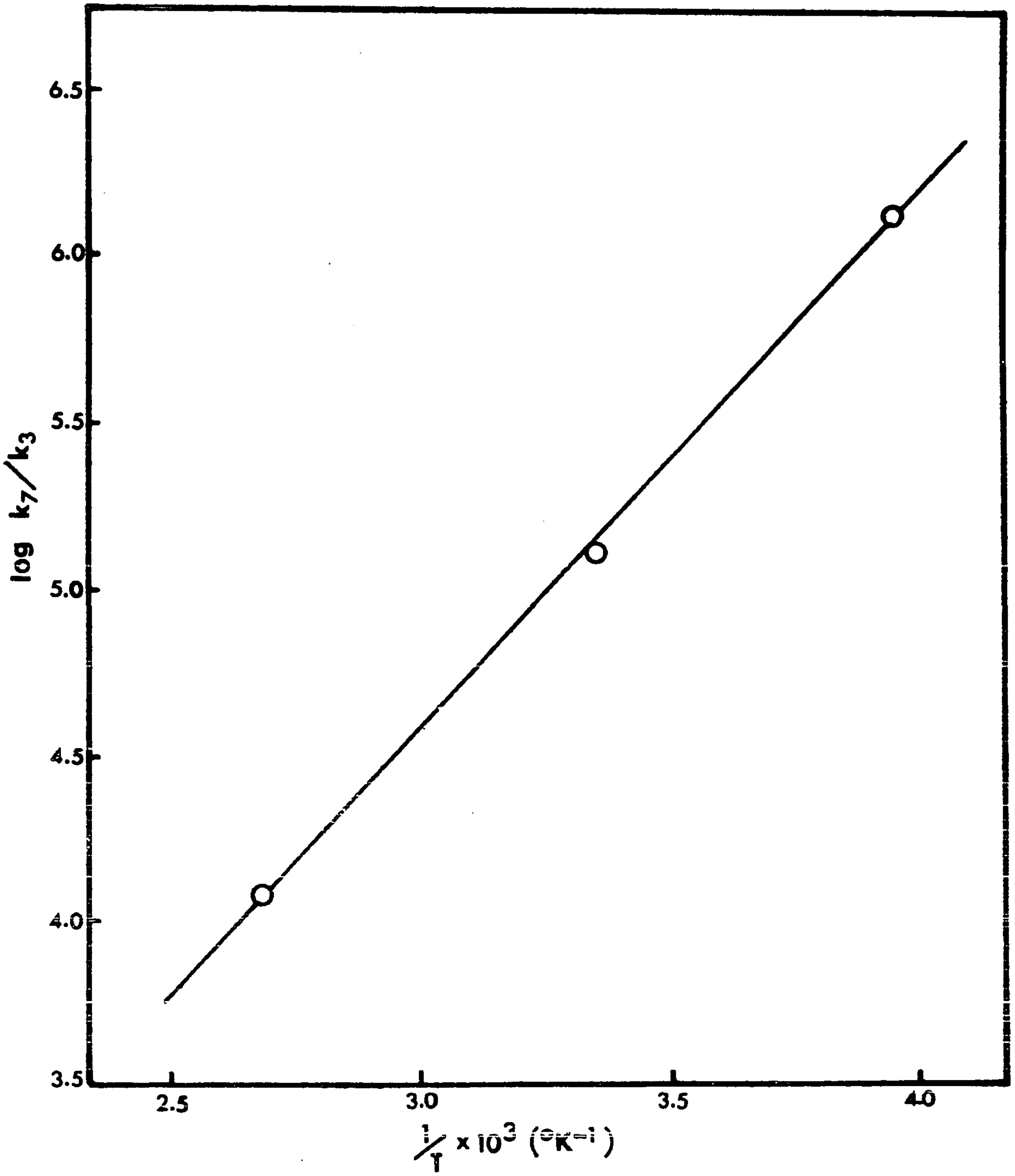


TABLE 17b

EFFECT OF TEMPERATURE ON k_7/k_3 FOR BUTENE-2

Temperature °K	$1/T \times 10^3$	$k_7/k_3 \times 10^{-5}$ liter $mole^{-1}$	$\log (k_7/k_3)$
253.2	3.949	17.54	6.244
298.2	3.353	1.70	5.231
373.2	2.680	0.145	4.161

The results in Table 17a show that the retardation of isomerization by oxygen is large at low temperatures and small at high temperatures. This observation may be explained in terms of two reactions,

$$X \xrightarrow{k_3} RS + \text{cis- or trans-Butene-2} \qquad (3)$$

$$X + O_2 \xrightarrow{k_7} XOO, \qquad (7)$$

for the disappearance of adduct radicals. Since the reaction of alkyl radicals with oxygen (reaction 7) is generally assumed to occur with zero activation energy, it may be assumed that $E_7 = 0$. Then by using the E_3-E_7 value obtained by the present study, E_3 for the decomposition of adduct radicals (reaction 3) is 7.1 kcal. Thus, for a given oxygen concentration, reactions 3 and 7 may be competitive at low temperatures, but at higher temperatures reaction 3 will dominate because $E_3 > E_7$, and the rate of isomerization becomes independent of oxygen.

From $(E_2$-$E_3)$ = -6.4 kcal which has been determined for butene-2 in Appendix 4, one obtains a second value for E_3 of 10.5 kcal, by assuming that E_2 for the adduct radical is the same as E_2 = 4.1 kcal for the methyl radical dehydrogenation of thiol (66). Therefore, E_3 estimated from E_3-E_7 is considerably smaller than E_3 estimated from E_2-E_3. This suggests that the adduct radicals may not be completely de-energized under the conditions used for this study (the total reactant pressure was 15 torr; see Table 17a). Thus it would be interesting to determine E_3-E_7 under the same conditions which were used to determine E_2-E_3 (the total reactant pressure was 200 torr; see Table 31 of Appendix 4).

However the rate expression for isomerization in the presence of oxygen is probably oversimplified. The main purpose was to show that the adduct radicals were reacting with oxygen, i.e. to show that co-oxidation was occurring. It has been assumed that all peroxy radicals transfer with thiol by the following reaction,

$$XOO + RSH \xrightarrow{k_9} XOOH + RS, \qquad (9)$$

but results which are to be presented in a subsequent section indicate that some peroxy radicals probably terminate heterogeneously on the wall of the reaction cell at 25°C. Therefore, results obtained from the isomerization of butene-2 in the presence of oxygen may not be entirely correct.

2. The Effect of Oxygen on Addition at 25°C

The problem of heterogeneous termination was first detected from the slight fogging of the cell surface during addition in the presence of oxygen, i.e. for the co-oxidation reaction. This observation was confirmed by the variation of the reaction rate with light intensity (see Table 18) which shows that the order dependence on initiation is almost first order for co-oxidation at 25°C.

TABLE 18

VARIATION OF LIGHT INTENSITY FOR CO-OXIDATION AT 25°C

Olefin	$R_0 \times 10^8$ no filter mole ℓ^{-1} sec^{-1}	$R_0 \times 10^8$ 26.6% T filter mole ℓ^{-1} sec^{-1}	Order Dependence on Initiation
Propylene	11.4	2.83	0.97
Butene-2	7.06	1.98	0.96
Acetylene	6.27	1.91	0.90
Methylacetylene	11.6	3.45	0.92
Allene	11.3	3.95	0.78
Butadiene-1,3	6.93	2.03	0.92
Butene-2 (no oxygen)	6.71	3.12	0.53

[Olefin] = [MeSH] = [Oxygen] = 2.69×10^{-3} moles liter^{-1}

Cell Length = 10 cm, $R_0 = -(\frac{1}{2})dP/dt$

As explained in section I(2), a first order dependence of the rate on initiation is observed for a heterogeneous termination process, while a half order dependence is observed for a homogeneous bimolecular termination process. The addition to butene-2 in the absence of oxygen (see last row of Table 18) gives a half order dependence on initiation.

The exact nature of the heterogeneous termination was not determined but it probably involved the wall termination of peroxy radicals. Although coating the vessel with boric acid by washing with a 5 per cent solution has been known to decrease the destruction of peroxy radicals on surfaces (64,65), no improvement was obtained for these reactions. Similarly, a reaction cell freshly washed with a 5 per cent HF solution or coated with dimethyldichlorosilane had no effect on termination at 25°C.

The stoichiometry for co-oxidation was established by following the disappearance of olefin by gas chromatography with n-butane as an internal standard. The pressure decrease during co-oxidation was found to be twice the rate of disappearance of olefin which is consistent with the over-all mechanism for co-oxidation,

$$CH_3SH + CH_2{=}CHR + O_2 \longrightarrow CH_3S\text{-}CH_2\text{-}CHR\text{-}OOH,$$

and it was necessary to correct all the rates obtained by pressure measurements by a factor of a half. Therefore, all the rates of co-oxidation, R_0, which are given in Table 19 to 27 are $-(\frac{1}{2})dP/dt$. Furthermore, only initial rates of co-oxidation were measured (the pressure changes were generally kept below 2 torr at 25°C) because at high conversions (above a pressure change of 10 torr) the reaction becomes autocatalytic. The nature of this autocatalysis was not determined but it probably resulted from the photolytic decomposition of the co-oxidation products.

The products obtained from the methanethiol-ethylene co-oxidation at 25°C were analyzed by mass spectrometry. A major peak at m/e = 108 was found which may be attributed to the hydroperoxide, $CH_3S\text{-}CH_2\text{-}CH_2\text{-}OOH$. From the cracking pattern it was concluded that the product was the hydroperoxide rather than a possible rearrangement product, $CH_3\text{-}SO\text{-}CH_2\text{-}CH_2\text{-}OH$. The addition product, $CH_3\text{-}S\text{-}CH_2CH_3$ (normally obtained in the absence of oxygen), was not detected.

3. Co-oxidation of Ethylene and Methanethiol

Homogeneous termination was obtained for the co-oxidation reaction at elevated temperatures. Table 19 indicates that the order dependence of the co-oxidation rate changes gradually from first to half order with increasing temperature; from these results it was concluded that homogeneous termination for coθoxidation occurs only above 125°C.

TABLE 19

VARIATION OF LIGHT INTENSITY FOR ETHYLENE CO-OXIDATION AT VARIOUS TEMPERATURES

Temperature °C	$R_0 \times 10^8$ no filter moles ℓ^{-1} sec^{-1}	$R_0 \times 10^8$ 26.6% T filter moles ℓ^{-1} sec^{-1}	Order Dependence on Initiation
50	16.5	5.32	0.91
75	20.5	7.52	0.76
100	20.2	8.32	0.68
1255	20.5	10.4	0.52
150	16.7	8.84	0.51

[Oxygen] = 1.08×10^{-3} moles liter^{-1}

[MeSH] = 5.38×10^{-3} moles liter^{-1}

[Ethylene] = 2.69×10^{-3} moles liter^{-1}

Cell Length = 2 cm (for all co-oxidation work)

The reason for observing a change in termination with temperature may be obtained by considering the effect of temperature on the RS radical population. In the presence of oxygen many of the adduct radicals are removed by oxygen as was shown by the competition of the terms k_3 and $k_7[O_2]$ during isomerization. However, it was also shown that $E_3 > E_7$. Therefore, increasing the temperature effectively increases the RS population by increasing reaction 3 over reaction 7. Consequently, high temperatures favour homogeneous termination by maintaining a high RS population even in the presence of oxygen.

The mechanism for co-oxidation under homogeneous RS-RS termination is shown in Figure 2. The results to be presented will show that co-oxidation above 125°C is reasonably consistent with this mechanism and that the rate of co-oxidation is given by the rate expression,

$$R_0 = -\left(\frac{d[O_2]}{dt}\right) = \frac{(\overline{r_i^{1/2}})}{(2k_4)^{1/2}}\left[\frac{k_1[E]k_7[O_2]}{k_3 + k_7[O_2]}\right],$$

which has been derived in Appendix 1.

The dependence of the co-oxidation rate on ethylene concentration is given in Table 20 and Graph 12 shows that a first order dependence was obtained only below 1.5×10^{-3} moles liter^{-1} of ethylene. Above this concentration the order dependence on ethylene falls off, while the order dependence on initiation goes up, which possibly indicates that heterogeneous termination returns at high olefin concentrations, even at high temperatures. This change in termination is consistent with a decrease in the RS radical population at high ethylene concentrations since ethylene removes RS radicals by a bimolecular reaction. Consequently, this investigation was carried out below 1.5×10^{-3} moles liter^{-1} of ethylene.

GRAPH 11

DEPENDENCE OF CO-OXIDATION RATE ON ETHYLENE CONCENTRATION AT 125°C

○ $(CH_3SH) = 9.68 \times 10^{-3}$ moles l^{-1} $(O_2) = 2.15 \times 10^{-3}$ moles l^{-1}

● $(CH_3SH) = 5.38 \times 10^{-3}$ moles l^{-1} $(O_2) = 1.08 \times 10^{-3}$ moles l^{-1}

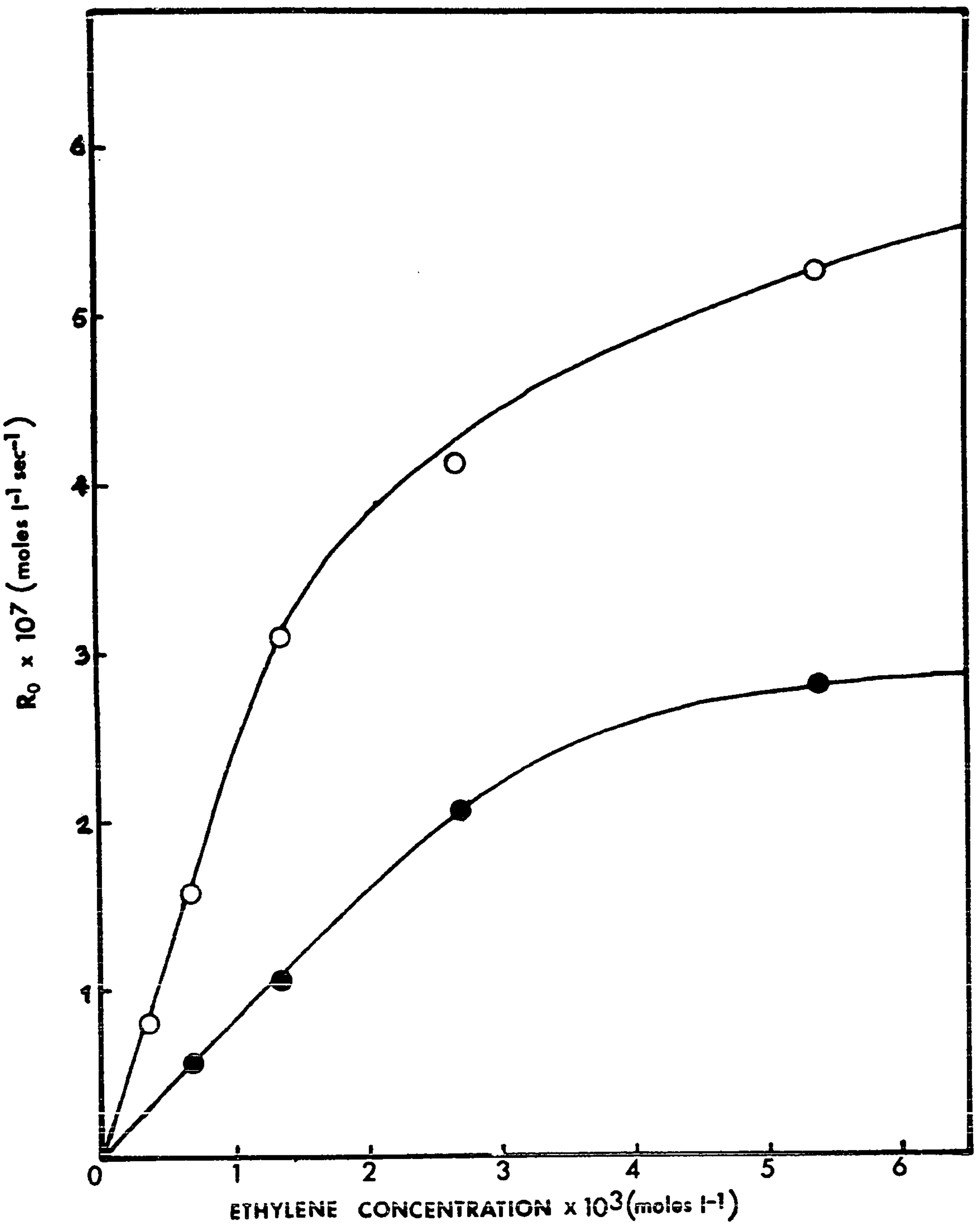


TABLE 20

CO-OXIDATION RATE DEPENDENCE ON ETHYLENE AT 125°C

Ethylene Concentration $x\ 10^3$ moles $liter^{-1}$	$R_0 \times 10^8$ no filter moles ℓ^{-1} sec^{-1}	$R_0 \times 10^8$ 26.6% T filter moles ℓ^{-1} sec^{-1}	Order Dependence on Initiation
0.34	8.0	3.8	0.56
0.67	15.8	7.6	0.55
1.35	30.9	14.6	0.53
2.69	41.2	——	——
5.38	52.5	26.0	0.53
10.8	64.0	28.0	0.62
$[CH_3SH] = 9.68 \times 10^{-3}$ moles ℓ^{-1}		$[O_2] = 2.15 \times 10^{-3}$ moles ℓ^{-1}	
0.67	5.9	2.9	0.48
1.35	10.5	5.8	0.45
2.69	20.5	10.5	0.52
5.38	27.9	12.9	0.57
$[CH_3SH] = 5.38 \times 10^{-3}$ moles ℓ^{-1}		$[O_2] = 1.08 \times 10^{-3}$ moles ℓ^{-1}	

The dependence of the co-oxidation rate on the oxygen concentration at several temperatures is given in Table 21 which shows an overall negative activation energy of -3.9 kcal at 2.15×10^{-3} moles $liter^{-1}$ of oxygen to -8.1 kcal at 0.27×10^{-3} moles $liter^{-1}$ of oxygen. This is consistent with the complex order dependence of the rate on oxygen. Moreover, the negative activation energy suggests a maximum temperature for co-oxidation; above 250°C the rate will be too small to measure.

TABLE 21

ETHYLENE CO-OXIDATION RATE DEPENDENCE ON OXYGEN CONCENTRATION

Oxygen Concentration $\times 10^4$ moles liter^{-1}	$R_0 \times 10^8$ (moles liter^{-1} sec^{-1})			
	125°C	145°C	155°C	165°C
2.69	3.98	2.54	2.00	1.56
3.76	——	3.78	2.76	2.22
4.03	5.56	——	——	——
5.38	——	4.84	3.90	2.76
5.78	7.54	——	——	——
8.08	9.68	6.76	——	4.72
10.8	10.5	——	——	——
21.5	17.2	15.5	12.5	11.1
53.8	22.9	24.7	——	21.0

[Ethylene] = 1.35×10^{-3} moles liter^{-1} = [E]

[CH_3SH] = 5.38×10^{-3} moles liter^{-1}

By using the reciprocal form of the rate expression,

$$\frac{1}{R_0} = \frac{(2k_4)^{\frac{1}{2}}}{(r_i^{\frac{1}{2}})} \frac{1}{k_1[E]} \left[\frac{k_3}{k_7[O_2]} + 1 \right],$$

a linear plot was obtained in Graph 12 from the data in Table 21 when $1/R_0$ was plotted against the reciprocal oxygen concentration. From this plot, a value of k_3/k_7 may be obtained from the ratio of the slope to the intercept, while k_1 may be obtained from the intercept alone, provided that the exact rate of initiation in the presence of oxygen is known.

GRAPH 12

DEPENDENCE OF ETHYLENE CO-OXIDATION RATE ON OXYGEN CONCENTRATION

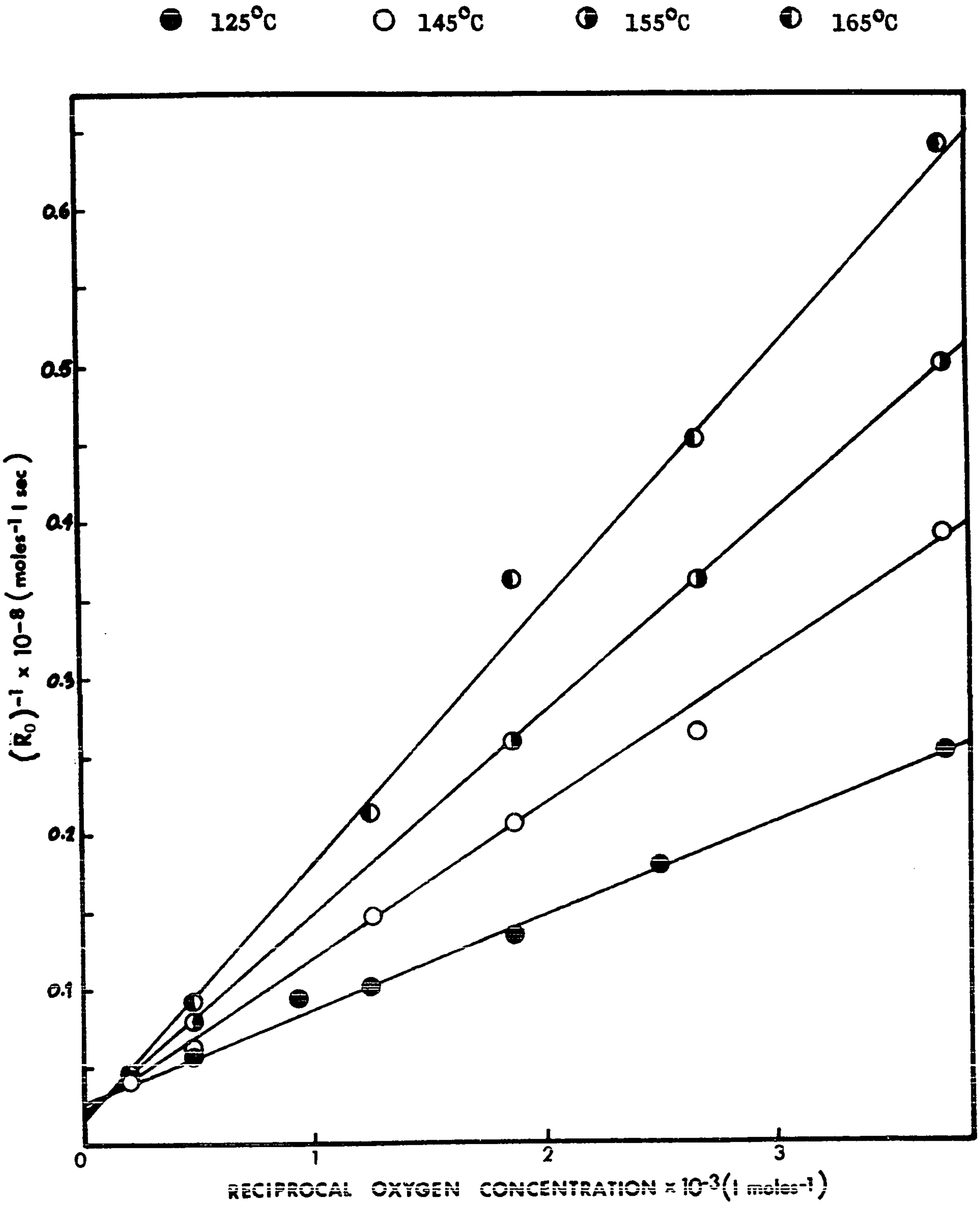


Table 22 contains k_3/k_7 values at various temperatures which have been determined from the ratio of the slope to the intercept of the reciprocal plots given in Graph 12.

TABLE 22

EFFECT OF TEMPERATURE ON k_3/k_7 FOR ETHYLENE CO-OXIDATION

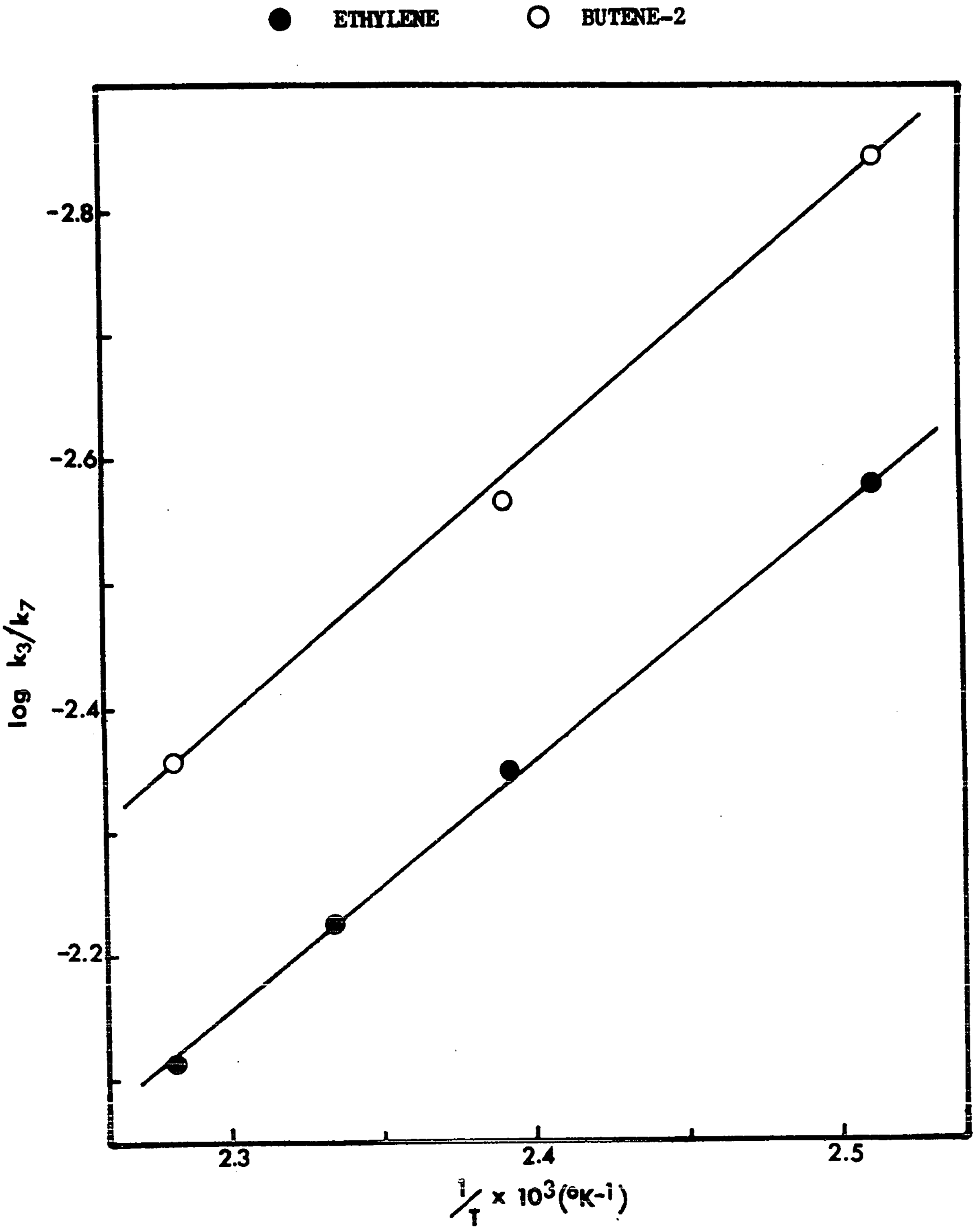
Temperature °K	$1/T \times 10^3$	$k_3/k_7 \times 10^3$ mole liter^{-1}	$\log (k_3/k_7)$
398.2	2.511	2.65	-2.577
418.2	2.391	4.48	-2.349
428.2	2.335	5.93	-2.227
438.2	2.282	7.71	-2.113

The Arrhenius plot of k_3/k_7 is shown in Graph 13 from which E_3-E_7 = 9.3 kcal. By making the reasonable assumption that E_7 is close to zero, E_3 is then about 9.3 kcal. From this value of E_3, E_2 may be estimated from the overall activation energy for addition to ethylene, $(E_1+E_2-E_3) = -5.0$ kcal, which has been determined in Appendix 4, since E_1 is zero. The estimated value of E_2 is 4.3 kcal which compares well with an activation energy of 4.1 kcal for the methyl radical dehydrogenation of methanethiol-d_3 (66).

By making use of $E_3 = 9.3$ kcal and by assuming a pre-exponential factor of 10^{12} sec^{-1}, one obtains a value of 8.3×10^6 liter mole^{-1} sec^{-1} for the decomposition rate constant, k_3, at 125°C. Then from the ratio k_3/k_7 at 125°C (see Table 22) one obtains $k_7 = 3.1 \times 10^9$ liter mole^{-1} sec^{-1} (reaction 7 is temperature independent) which may be

GRAPH 13

ARRHENIUS PLOT OF k_3/k_7 FOR CO-OXIDATION



compared to k = 4.2×10^9 liter $mole^{-1}$ sec^{-1} for the reaction of ethyl radicals with oxygen (63). Similarly, by estimating k_3 at 25°C (1.7×10^5 liter $mole^{-1}$ sec^{-1}) and by making use of $k_1k_2/k_3 = 2.0 \times 10^6$ $liter^2$ $mole^{-2}$ sec^{-1} and $k_1 = 4.8 \times 10^5$ liter $mole^{-1}$ sec^{-1} (24,68), one obtains $k_2 = 7.0 \times 10^5$ liter $mole^{-1}$ sec^{-1} (the transfer rate constant, see Figure 2); this value of k_2 may be compared to 1.1×10^5 liter $mole^{-1}$ sec^{-1} for the methyl radical dehydrogenation of thiol (66).

The dependence of rate of co-oxidation on thiol concentration as shown in Table 23 shows that the rate is almost independent of thiol, which is consistent with the derived rate expression. However, the initiation rates were obtained at 25°C in the absence of oxygen and do not appear to be applicable to the reaction at 25°C in the presence of oxygen.

TABLE 23

ETHYLENE CO-OXIDATION RATE DEPENDENCE ON THIOL CONCENTRATION AT 125°C

Methanethiol Concentration $\times 10^3$ moles $liter^{-1}$	R_0 $\times 10^8$ moles $liter^{-1}$ sec^{-1}	$\frac{R_0}{(r_i^{1/2})}$ $\times 10^4$
1.35	3.04	1.01
3.23	9.44	1.86
5.38	14.1	2.34
7.51	16.3	2.46
9.68	18.1	2.46

[Ethylene] = 1.35×10^{-3} moles $liter^{-1}$

[Oxygen] = 1.08×10^{-3} moles $liter^{-1}$

The difficulty in using rates of initiation which have been obtained in the absence of oxygen was first realized when unreasonably short chain lengths were calculated for co-oxidation. The average chain length which may be calculated for the rates in Table 23 is only 0.4, when the initiation rates obtained in the absence of oxygen are used. This difficulty was confirmed when the intercept of the reciprocal plot (Graph 12) failed to give the correct value of k_1 for ethylene; a value of 3.4×10^4 liter mole^{-1} sec^{-1} was obtained for k_1 which may be compared to a known value of 4.8×10^5 liter mole^{-1} sec^{-1} (23,68). These results suggest that the actual rate of initiation is lower than the calculated rate of initiation. Therefore, the actual chain lengths must be greater than the calculated chain lengths. Apparently, the presence of oxygen has affected the rate of initiation, but a conclusive explanation is not possible without further investigation. The values of k_3/k_7 which were obtained from Graph 12, however, are probably not affected because the rate of initiation is not directly involved, i.e. the initiation term, $(r_i^{1/2})$, cancels out in the ratio of the slope to the intercept.

Thus, if it is assumed that oxygen decreases the rate of initiation by a constant factor at all thiol concentrations, the conclusion that the rate of co-oxidation is independent of thiol concentration (based on the results of Table 23) appears to be reasonable.

4. Co-oxidation of Butene-2 and Methanethiol

The kinetics of cis-butene-2 co-oxidation was found to be similar to the co-oxidation of ethylene with the exception of a fast cis-trans isomerization of butene-2 which preceeds the co-oxidation reaction. The problem of heterogeneous termination was again overcome by increasing the temperature. Table 18 shows that the order dependence on initiation for butene-2 co-oxidation was 0.96 at 25°C; this order dependence changed to 0.59 at 100°C and decreased to 0.51 at 125°C. Consequently, the lowest temperature of this investigation was 125°C.

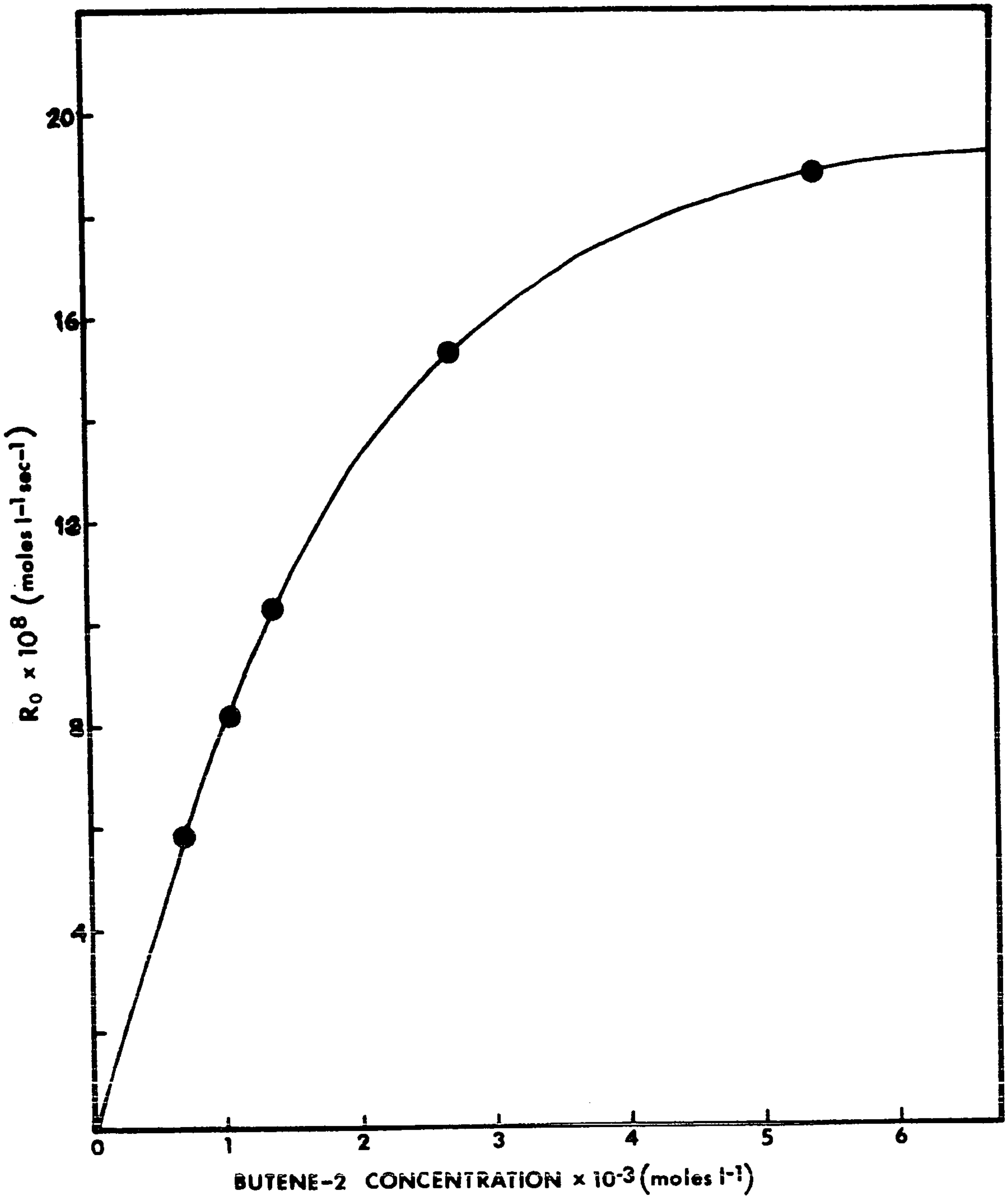
The results of Table 24 indicate, that up to a concentration of 1.5×10^{-3} moles liter^{-1} of butene-2, the dependence of the rate of co-oxidation is first order. Graph 14 indicates that above this concentration the rate falls off (a similar fall off was observed for the co-oxidation of ethylene; see Graph 11). Therefore, this study was carried out below 1.5×10^{-3} moles liter^{-1} of butene-2.

The dependence of the co-oxidation rate on oxygen concentration at various temperatures is given in Table 25 for which the overall activation energy varies from -5.0 kcal at 5.38×10^{-3} moles liter^{-1} of oxygen to -9.2.kcal at 0.27×10^{-3} moles liter^{-1} of oxygen.

Using the reciprocal form of the co-oxidation rate equation, linear plots were obtained in Graph 15 when $1/R_0$ was plotted against the reciprocal oxygen concentration. From the ratio of the slope to the intercept of these plots, the rate constant ratio k_3/k_7 for various temperatures was determined as shown in Table 26. Similar values have been obtained for the co-oxidation of ethylene in part 3.

GRAPH 14

DEPENDENCE OF CO-OXIDATION RATE ON BUTENE-2 CONCENTRATION AT 125°C



GRAPH 15

DEPENDENCE OF BUTENE-2 CO-OXIDATION RATE ON OXYGEN CONCENTRATION

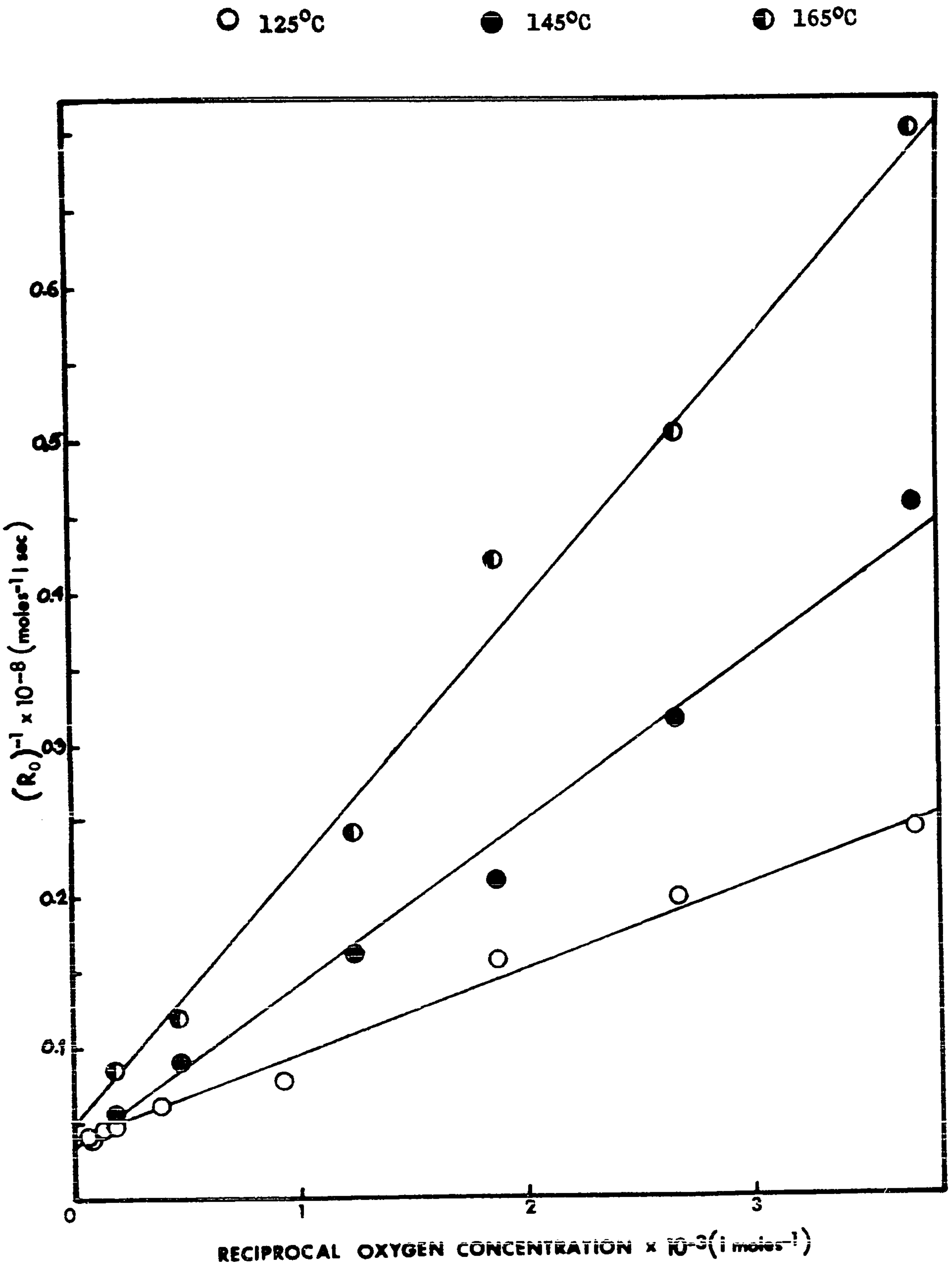


TABLE 24

CO-OXIDATION RATE DEPENDENCE ON BUTENE-2 AT 125°C

Butene-2 Concentration $\times 10^3$ moles liter^{-1}	R_0 $\times 10^8$ moles liter^{-1} sec^{-1}
0.67	5.88
1.01	8.24
1.35	10.3
2.69	15.4
5.38	18.9
10.8	21.5

$[CH_3SH] = 2.69 \times 10^{-3}$ moles liter^{-1}

$[\text{Oxygen}] = 1.08 \times 10^{-3}$moles liter^{-1}

The Arrhenius plot of k_3/k_7 for butene-2 co-oxidation is shown in Graph 13 and the value obtained for E_3-E_7 was 9.8 kcal. Again, by assuming that E_1 and E_7 are close to zero, E_2 may be estimated from E_3-E_7 and the overall activation energy for addition to butene-2, $(E_1+E_2-E_3) = -6.4$ kcal, as obtained from Appendix 4. The estimated value of E_2 is then 3.4 kcal which may be compared to a value of 4.3 kcal obtained for ethylene co-oxidation.

By assuming a pre-exponential factor of 10^{12} sec^{-1} and taking $E_3 = 9.8$ kcal (by assuming $E_7 = 0$), one obtains a value of 4.5×10^6 liter mole^{-1} sec^{-1} for k_3 at 125°C. Then from the ratio k_3/k_7 at 125°C (see Table 26) one obtains $k_7 = 3.2 \times 10^9$ liter mole^{-1} sec^{-1} for butene-2 which compares well with a value of 3.1×10^9 liter

TABLE 25

BUTENE-2 CO-OXIDATION RATE DEPENDENCE ON OXYGEN CONCENTRATION

Oxygen Concentration x 10^4 moles $liter^{-1}$	$R_0 \times 10^8$ (moles $liter^{-1}$ sec^{-1}) 125°C	145°C	165°C
2.69	4.10	2.18	1.42
3.76	5.02	3.16	1.98
5.38	6.34	4.76	2.36
8.08	——	6.14	4.16
10.8	12.8	——	——
21.5	——	10.9	8.24
26.9	16.4	——	——
53.8	20.8	17.6	11.8
80.7	21.9	——	——
107.6	26.8	——	——
161.3	24.6	——	——

[Butene-2] = 1.35×10^{-3} moles $liter^{-1}$

$[CH_3SH] = 5.38 \times 10^{-3}$ moles $liter^{-1}$

TABLE 26

EFFECT OF TEMPERATURE ON k_3/k_7 FOR BUTENE-2 CO-OXIDATION

Temperature °K	$1/T \times 10^3$	$k_3/k_7 \times 10^3$ mole $liter^{-1}$	log (k_3/k_7)
398.2	2.511	1.43	2.845
418.2	2.391	2.73	2.564
438.2	2.282	4.37	2.359

TABLE 27

BUTENE-2 CO-OXIDATION RATE DEPENDENCE ON THIOL CONCENTRATION AT 125°C

Methanethiol Concentration $\times 10^3$ moles liter^{-1}	R_0 $\times 10^8$ moles liter^{-1} sec^{-1}	$\frac{R_0}{\overline{(r_i^{1/2})}}$ $\times 10^4$
1.08	4.12	1.37
3.23	8.04	1.58
5.38	10.3	1.70
7.53	11.0	1.69
9.68	13.4	1.80

[Butene-2] = 1.35×10^{-3} moles liter^{-1}

[Oxygen] = 1.08×10^{-3} moles liter^{-1}

mole^{-1} sec^{-1} obtained for ethylene. Similarly, by estimating k_3 at 25°C (6.8×10^4 liter mole^{-1} sec^{-1}) and by making use of $k_1k_2/k_3 = 1.6 \times 10^6$ liter^2 mole^{-2} sec^{-1} and $k_1 = 1.6 \times 10^6$ liter mole^{-1} sec^{-1} (24,68), one obtains $k_2 = 6.4 \times 10^4$ liter mole^{-1} sec^{-1}; this value of k_2 is somewhat smaller than a value of 7.0×10^5 calculated for ethylene.

The constant value of $R_0/\overline{(r_i^{1/2})}$ in Table 27 shows that the rate of co-oxidation is almost independent of thiol concentration. However, the rates of initiation during butene-2 co-oxidation have also been affected by the presence of oxygen and the chain lengths for the rates given in Table 27 are unreasonably short (the average chain length being 0.3). Thus it has been assumed in Table 27 that oxygen affects the rate of initiation by a constant factor.

Due to the effect of oxygen on the rate of initiation, the intercept of the reciprocal plot (Graph 15) failed to give the correct value of k_1 for butene-2; a value of 2.1×10^4 liter mole^{-1} sec^{-1} was obtained from the intercept which compares poorly with a known value of 1.6×10^6 liter mole^{-1} sec^{-1} (23,68). However, as explained for the co-oxidation of ethylene, the k_3/k_7 values are probably unaffected. Moreover, there is a fair agreement between $k_3/k_7 = 2.4 \times 10^{-5}$ mole liter^{-1} (reduced to 25°C) obtained by this method and a value of 0.9×10^{-5} mole liter^{-1} at 25°C obtained from isomerization (see Table 17b).

The values of k_3, k_7, and k_2 which have been estimated from the kinetics of co-oxidation are summarized in Table 28; k_1 and k_1k_2/k_3 values obtained from other studies are also included.

TABLE 28

RATE CONSTANTS FOR REACTION WITH METHANETHIOL AT 25°C

Rate Constant	Ethylene	Butene-2
k_1*(liter mole^{-1} sec^{-1})	4.8×10^5 $E_1 = 0$	16×10^5** $E_1 = 0$
k_2 (liter mole^{-1} sec^{-1})	7.0×10^5 $E_2 = 4.3$	6.4×10^4 $E_2 = 3.4$
k_3 (sec^{-1})	1.7×10^5 $E_3 = 9.3$	6.8×10^4 $E_3 = 9.8$
k_7 (liter mole^{-1} sec^{-1})	3.1×10^9 $E_7 \simeq 0$	3.2×10^9 $E_7 \simeq 0$
k_1k_2/k_3* (liter^2 mole^{-2} sec^{-1})	20×10^5 $(E_1+E_2-E_3) = -6.4$	15×10^5 $(E_1+E_2-E_3) = -5.4$

** cis-trans equilibrium weighted rate constant; reference (24)
* taken from reference (60).....all E values in units of kcal

Unfortunately, it was not possible to isolate thiyl radical attack constants for olefins from the kinetics of co-oxidation, but the estimated values of k_3 and k_2 are extremely useful when discussing the reaction of thiols and olefins. The rate constant, k_7, which was estimated by this study, is important because it illustrates the rapidity of the reaction of oxygen with alkyl radicals (this reaction is considered to be a radical-radical reaction because oxygen behaves as a biradical); there have been very few determinations of this rate constant.

The greatest significance of this co-oxidation study, however, is in the values obtained for the ratio, k_3/k_7. From this ratio it was possible to determine the conditions under which $k_7[O_2] >> k_3$. Under such conditions, every adduct radical reacts with oxygen rather than decomposing by reaction 3. These conditions were used to develop a new technique for the determination of relative reactivities of olefins towards thiyl radicals. The essentials of this technique are described in the next section.

VI RELATIVE REACTIVITIES

In this chapter a new method is described for the determination of relative reactivities of olefins towards thiyl radicals. Essentially, the method involves the competitive co-oxidation of several olefins under the proper conditions during which the reversibility of thiyl radical addition becomes negligible. The criterion for such conditions is that, $k_7[O_2] >> k_3$, in the following competitive reactions:

$$A + RS \underset{k_{3a}}{\overset{k_{1a}}{\rightleftharpoons}} X_a \xrightarrow{k_{7a}[O_2]} X_aOO \xrightarrow{k_{8a}[RSH]} \text{products} + RS$$

$$B + RS \underset{k_{3b}}{\overset{k_{1b}}{\rightleftharpoons}} X_b \xrightarrow{k_{7b}[O_2]} X_bOO \xrightarrow{k_{8b}[RSH]} \text{products} + RS$$

$$C + RS \underset{k_{3c}}{\overset{k_{1c}}{\rightleftharpoons}} X_c \xrightarrow{k_{7c}[O_2]} X_cOO \xrightarrow{k_{8c}[RSH]} \text{products} + RS$$

where A, B, and C, are olefins in a mixture competing for thiyl radicals, and k_{1a}, k_{1b}, and k_{1c}, are the corresponding thiyl radical attack constants. Then by assuming that olefins disappear only by reaction with thiyl radicals, it is possible to obtain relative thiyl attack constants from the following relationships:

$$\frac{k_{1a}}{k_{1b}} = \frac{[B]}{[A]}\frac{R_a}{R_b}, \quad \frac{k_{1a}}{k_{1c}} = \frac{[C]}{[A]}\frac{R_a}{R_c}, \quad \text{and} \quad \frac{k_{1b}}{k_{1c}} = \frac{[C]}{[B]}\frac{R_b}{R_c},$$

where R_a, R_b, and R_c, are the rates of disappearance of the corresponding olefins, and [A], [B], and [C], are the corresponding concentrations.

This method is unique in that it depends only on the competition of olefins for available thiyl radicals (provided that the criterion, $k_7[O_2] >> k_3$, is maintained) and that it does not require an exact knowledge of initiation or termination. These features are most fortunate because in chapter V it was shown that initiation is difficult to establish during co-oxidation and that heterogeneous termination predominates at the temperature used in this investigation.

1. Determination of Relative Reactivities

The procedure consisted of photolyzing a mixture of gases containing at least two olefins, n-butane (an unreactive internal standard), methanethiol, and oxygen. The criterion that $k_7[O_2] >> k_3$ was favoured by high oxygen concentrations (2.94×10^{-2} mole liter^{-1}) and low temperatures (0°C for all results), i.e. $E_7 \approx 0$ while $E_3 = 9.8$ kcal. Under these conditions $k_7[O_2]/k_3$ is at least 10^3. Equimolar quantities of each olefin and n-butane were used (2.94×10^{-4} mole liter^{-1}) so that relative attack constants were directly proportional to the relative rates of olefin disappearance; conversions were kept to about 10 per cent. The thiol concentration was kept high at 5.87×10^{-3} mole liter^{-1} to assure transfer through thiol and not n-butane.

Hydrocarbon analysis was carried out by gas chromatography; the equipment has been described previously in part 6 of the experimental section. Then by assuming that n-butane is unreactive, the reacted mixture was compared to the unreacted mixture to determine the disappearance of olefin. Analysis of the unreacted portion served to calibrate the gas chromatograph; the use of n-butane was necessary to apply the calibration to the reacted mixture. Gas analysis was carried out directly from the reaction vessel (a 5 cm diameter spherical fused quartz cell) which was demountable from the main gas manifold. This sampling technique was employed when analysis carried out from small transfer tubes gave unreproducible results.

The relative reactivities of several olefins towards CH_3S radicals (the rate of addition to ethylene taken as unity) which have been obtained by the co-oxidation method are: methylacetylene 0.92 ± 0.20(3), ethylene 1.00, trans-butene-2 1.96 ± 0.75(3), propylene 2.42 ± 0.24(3), cis-butene-2 4.13 ± 0.72(10), isobutene 4.45 ± 0.84(4), with 70 per cent confidence limits, and where the number in brackets is the number of experimental determinations. These results are also summarized in the first column of Table 29. However, it should be pointed out, that not all olefins were reacted simultaneously because the column (a 300 foot dimethylsulfolane capillary column, operating at 0°C) was not capable of a complete separation, but ethylene was present in each case. The rather large errors for these results are thought to be primarily due to analytical difficulties; considerable difficulty was encountered in reproducing sample analysis, especially when the molecular weights of the olefins were different.

The relative reactivities of other radicals towards olefins, which are useful in the following discussions, are also given in Table 29.

TABLE 29

COMPARISON OF RELATIVE REACTIVITIES

Olefin	CH_3S (0°C) (this work)[a]	$S(^3P)$ (25°C)[b]	$O(^3P)$ (25°C)[b]	H (25°C)[b]	CF_3 (65°C)[b]	CH_3 (180°C)[b]	Ionization Potential (eV)
Acetylene	0.17(d)	——	——	——	0.19	——	11.41
Methylacetylene	0.92 ± 0.20	——	——	——	0.48	——	10.36
Ethylene	1.00	1.0	1.0	1.0	1.0	1.00	10.51
trans-Butene-2	1.96 ± 1.16	19	28	1.1	1.0	0.33	9.25
Allene	2.24 ± 0.75	——	——	——	——	——	10.19
Propylene	2.42 ± 0.24	6.8	5.8	1.8	1.2	0.7	9.73
cis-Butene-2	4.13 ± 0.72	16	24	0.8	0.9	0.23	9.29
Isobutene	4.45 ± 0.84	51	25	4.4	3.7	1.1	9.23
Butadiene-1,3	105(e)	93	24	8.7	8.7	12	8.75
2-Methylbutene-2	——————	92	79	——	——	0.32	8.80
2,3-Dimethylbutene-2	——————	128	102	1.5	1.3	0.20	8.30
Electron Affinity (eV)[c]	≈2.9	2.07	1.47	0.75	≈2.0	1.08	

(a) 70% confidence limits, (b) ref. 70, (c) ref. 58, (d) absolute value, (e) inhibition method.

2. Relative Reactivities of cis- and trans-Butene-2

The results in Table 29 show that cis-butene-2 is about two times more reactive than trans-butene-2 towards CH_3S radicals, i.e. $k_{1c}/k_{1t} = 2.11$, but the experimental error for the butene-2 results obtained relative to ethylene are rather high (see Table 29). A much better value for k_{1c}/k_{1t} was obtained directly from the rates of disappearance of cis- and trans-butene-2 during co-oxidation (relative to each other) from which $k_{1c}/k_{1t} = 2.07 \pm 0.20$ (70 per cent confidence limits, using 4 experimental determinations). Although the magnitudes are similar, the latter value for k_{1c}/k_{1t} is much more acceptable, considering the small error, and is the value used in further discussions.

A value of ρ_3 for butene-2 (previously defined as the probability factor that the trans olefin will be formed during the decomposition of X) may be derived from the ratio k_{1c}/k_{1t} by making use of the equilibrium constant, K, which has been defined (22,23) as,

$$K = \frac{[T]_{eq}}{[C]_{eq}} = \frac{k_{1c}\rho_3}{k_{1t}(1-\rho_3)} ,$$

where K = 3.2 at 25°C (71). Then, making use of the ratio $k_{1c}/k_{1t} = 2.07$, a value of 0.61 was obtained for ρ_3.

It was this value of ρ_3 which was applied in part II(2) to establish the magnitude of k_{1b}/k_{1c} (the relative attack constants of butadiene-1,3 and cis-butene-2) from the ratio $k_{1b}/\rho_3 k_{1c}$.

Also, from previous isomerization kinetics (23,69), $\rho_3 k_{1c}$ has been reported as 1.6×10^6 liter mole^{-1} sec^{-1}, and now that $\rho_3 = 0.61$, $k_{1c} = 2.6 \times 10^6$ liter mole^{-1} sec^{-1} (the absolute attack constant for cis-butene-2); the same study gives a value of 4.8 x 10^5 liter $mole^{-1}$ sec^{-1} for the attack constant for ethylene. Hence, from absolute attack constants, the relative reactivity of cis-butene-2 to ethylene is 5.4, which compares reasonably well with a value of 4.1 obtained by the present co-oxidation method. Unfortunately, other absolute attack constants are not available as a further test of the co-oxidation method.

3. Correlation of Relative Reactivities

The factors which govern the relative reactivity of thiyl radicals towards various olefins are not clearly understood, primarily due to a lack of experimental information. During the course of this study primary emphasis was on establishing a method for determining relative reactivities. Unfortunately, of the mono-olefins studied, the difference in the rates are small, and in view of the experimental errors (see Table 29), caution must be used in discussing the trends observed. Moreover, a need to extend this study to more highly substituted mono-olefins (with electron-withdrawing groups as well) is now recognized. With this in mind, a tentative explanation of the over-all trend in reactivity will be offered.

Recently, Mieville (22) has obtained very convincing evidence that the addition of CH_3S radicals to cis-butene-2 proceeds with zero activation energy ($E_a = 0.050 \pm 0.046$ kcal). It was then concluded that differences in reactivities of various olefins towards CH_3S should be attributed solely to differences in pre-exponential factors. This unique feature of thiyl radical addition is in contrast to the addition of H, CH_3, O, or CF_3 radicals to olefins all of which exhibit small activation energies. But it should be pointed out that activation energies of CH_3S addition to olefins other than for cis-butene-2 have not yet been determined. The present view, that thiyl radical addition to other mono-olefins proceeds with zero activation energy, is based on structural similarities of the olefins and adduct radicals to that of cis-butene-2. No activation energy is expected for conjugated olefins, such as butadiene, from which a more stable adduct radical is obtained.

The absence of an activation energy for thiyl radical addition to olefins represents excellent grounds for postulating the formation of a π-complex. This implies an interaction between thiyl radicals and the double bond at relatively large distances where the direct effects of substituents are still small. In this case, one would expect to find a constancy of pre-exponential factors in attack constants. The relatively little spread in reactivities from ethylene to isobutene for thiyl radicals (see Table 29) certainly bears this out. But the main argument for π-complexing is that only long-range attractive forces are involved and that the exothermic heat of π-complex formation may be applied against the normal activation energy of addition. Under such conditions one could expect to observe reduced or zero activation energies such as those observed for the addition of thiyl radicals.

The formation of a π-complex is favoured by high electron affinity of the radical and low ionization potential of the olefin. If one takes the electron affinity as a measure of electrophilicity, then the following decreasing order of electrophilic radicals is obtained (the value in brackets being the electron affinity in units of electron-volt): Cl(3.8), Br(3.5), CH_3S(~2.9), S(2.1), CF_3(~2.0), and O(1.5). The electrophilic character of CH_3S is also evident from the increase in reactivity with decreasing ionization potential of the olefin (see Table 29), in which case, the ionization potential is a measure of the electron-donating power of the olefin.

There is reasonable evidence that radicals are capable of π-complexing. The work of Russell(71) suggests that Cl-atoms form π-complexes with aromatic compounds. Further evidence has been obtained by Abell and Piette (72) for Br-atoms from electron-spin resonance during the addition to butene-2; the spectrum for the bromoalkyl radical was found consistent with a symmetrical or bridged structure. Unfortunately no direct evidence of π-complex formation for thiyl radicals is presently available. However an interesting analogy may be drawn between CH_3S radicals and iodine, since iodine forms a well characterized π-complex with benzene (73). From the similarity of ionization potentials, benzene (9.2 eV) and butene-2 (9.3 eV), and the similarity of electron affinities, I_2 (2.4 eV) and CH_3S (2.9 eV), it is possible to make several inferences. For instance, from the strength of the iodine-benzene complex (74), i.e. the enthalpy of formation of 1.3 kcal, one may expect a comparable or even larger interaction for CH_3S with butene-2, especially since the electron affinity of I_2 is thought to be over-estimated, and is possibly as low as 1.8 eV. Also from the nearest approach of I_2 to benzene, 3.5 A, one obtains an appreciation of the internuclear separations involved during π-complexing. Moreover, other studies (75,76) show that the stability of iodine complexes with alkenes falls between those of tri- and tetra-alkylbenzenes, while a more recent study (77) gives the stability of the iodine-cyclohexene complex as 2.2 kcal. And since CH_3S is undoubtedly more electrophilic than iodine, there is no reason to doubt that CH_3S is capable of forming π-complexes with olefins.

It should be stressed however, that the occurrence of π-complexing at large internuclear separations does not exclude the formation of a final σ-complex after stronger short-range forces become important, i.e. the thiyl radical being attached to a particular carbon atom of the C=C bond. In fact, the rapid isomerization of butene-2 indicates that a σ-type adduct radical is ultimately formed, since isomerization requires free rotation about the original C=C bond.

By considering absolute thiyl attack constants in terms of transition-state theory, one must conclude that a σ-type adduct radical is formed. If the final adduct radical was a π-complex, a loose transition-state complex which resembles the reactants would be expected; thus the entropy of activation for addition would be small and the pre-exponential factor for the attack constant would be large. On the other hand, the formation of a σ-type adduct radical would require a tight transition-state complex which would resemble the product; the entropy of activation should then be close to the thermodynamic entropy change for the process. Assuming zero activation energies, the entropy of activation calculated from absolute thiyl radical attack constants (23,68) for ethylene and butene-2 are -25.2 cal/mole-degree and -22.9 cal/mole-degree, respectively, when the standard state is taken as 1 mole/liter. The calculated thermodynamic entropy changes (converted to a standard state of unit concentration) for the attack step are -20.6 and -25.3 cal/mole-degree for ethylene and butene-2, respectively. Then, in view of the fact that the entropy of activation is close to the thermodynamic entropy change for the attack step, one must conclude that the transition-state resembles the final adduct radical. Thus the attack step proceeds through a σ-type transition-state.

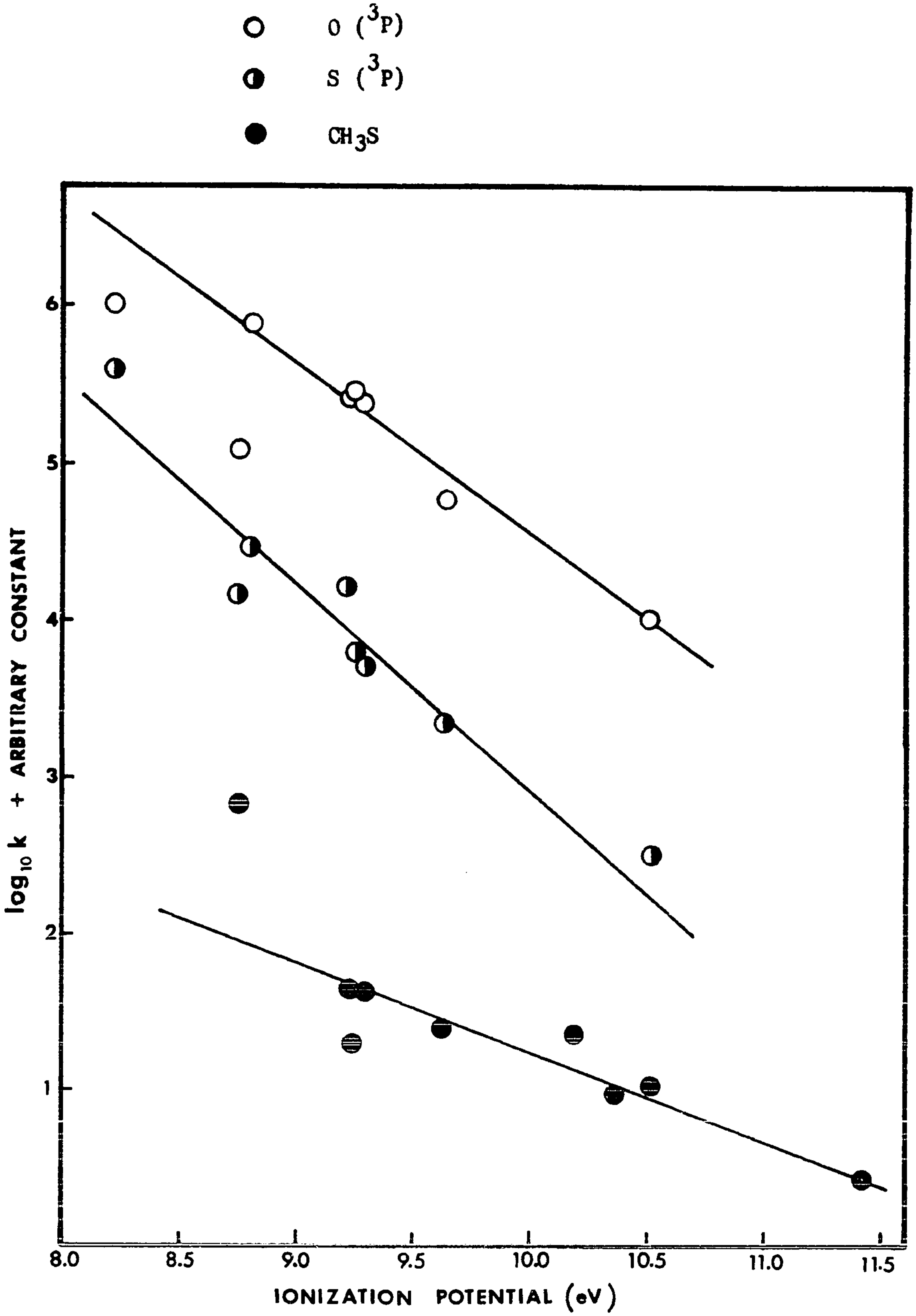
The reason for having considered π-complex formation at large internuclear separations was to explain the zero activation energy for addition. But in a recent review article (78) it was pointed out that the large covalent radius of sulfur could result in low activation energies for bimolecular thiyl radical reactions. The C-S bond length is about 0.3 A greater than the C-C bond length and about 0.4 A greater than the C-O bond length (both sulfur and oxygen being in the bivalent state). This means that the steric accessibility of a reaction center for thiyl radicals is much greater than for other radicals, i.e. the repulsion between the sulfur atom and nonbonded groups are smaller. Perhaps this is the reason for observing small activation energies of 2 to 6 kcal for the addition of O, CH_3, and CF_3, to olefins while CH_3S exhibits no activation energy.

For the reaction of oxygen atoms with olefins, Cvetanovic (56, 79), has concluded that the formation of a π-complex is the rate determining step and that the localization of the oxygen atom on a specific carbon atom occurs after passing over a π-type activated complex. The argument was based primarily on the observation that the attack rate constant did not depend on the position of methyl substituents but only on their number, and also that the pre-exponential factor for addition was approximately constant for all olefins. Moreover, a plot of ionization potential of various olefins against the log of the corresponding attack constants resulted in a linear plot; the ionization potential represents the availability of electrons when the olefin is approached by an electrophilic reagent. This type of plot is shown in Graph 16 for O, S, and CH_3S radicals, where the ionization potentials and relative rate constants are those contained in Table 29 (a statistical factor of ½ was given to butadiene-1,3 because it possesses two C=C bonds). It may be seen that CH_3S radicals and S-atoms result in linear plots as well. But the relative reactivity of O-atoms towards olefins has been ascribed to differences in activation energies while for CH_3S it has been ascribed to differences in pre-exponential factors. Therefore, it appears that such plots are not conclusive evidence for postulating π-complex formation.

It has been argued by Szwarc (80) that the addition of O-atoms to olefins must involve a specific carbon atom and that the transition-state resembles a σ-complex. Szwarc finds the activation energy, suggested by Cvetanovic for π-complex formation, highly improbable since it is difficult to imagine repulsive forces with a longer range than the attractive forces responsible for π-complex formation. Szwarc has reaffirmed this view during a recent investigation of the addition of CF_3 radicals (81) in which he concludes that a σ- rather than a π-type transition-state also describes the addition of CF_3 to olefins.

GRAPH 16

PLOT OF LOG k AGAINST THE IONIZATION POTENTIAL



In general, it may be concluded that the transition-state for the addition of electrophilic radicals to olefins is best described by a tight transition-state. Benson (82) feels that the rehybridization of the olefin electrons from sp^2 to sp^3 during the addition of CH_3 to mono-olefins required a relatively close contact between the reacting partners. This apparently applies for electrophilic radicals as well.

The reactivity of acetylene may also be rationalized in terms of a σ-type transition-state. As it was shown in section IV(4), ethylene is about 6 times more reactive than acetylene towards thiyl radicals. Since the 2s orbital of carbon has a smaller mean radius than the 2p orbitals, one finds that the sp^x hybrid orbitals are shorter, the more s-character they contain. The single bond covalent radii of carbon in various states of hybridization are: sp^3, 0.77 A; sp^2, 0.74 A; and sp, 0.70 A. Consequently, the incipient C-S bond for the addition to acetylene is about 0.03 A shorter than the incipient C-S bond for the addition to ethylene. Therefore, one would expect a tighter transition-state and a corresponding larger (negative) entropy of activation for the addition to acetylene. Then, because the addition to both occurs with essentially zero activation energy, one finds ethylene more reactive than acetylene.

Of the other olefins studied, with the exception of butadiene, the range of relative reactivities is not great (see Table 29). Nevertheless, one can arrive at several conclusions about the addition of thiyl radicals to these olefins by considering the trends in the data. However, one should recall, through-out this discussion, that the addition to substituted olefins occurs exclusively in an anti-Markownikoff manner, i.e. the thiyl radical will attack an unsymmetrically substituted olefin at the least substituted carbon which results in the formation of the more stable of the two possible adduct radicals. Then a methyl substituent introduced on the carbon adjacent to the reaction center leads to a 2-fold increase in reactivity (compare ethylene, propylene, and isobutene). Similarly, a methyl substituent introduced at the reaction center leads to about a 2-fold increase in reactivity (compare propylene with cis-butene-2). But a substituent located at the reaction center also exhibits a steric effect (compare propylene, trans-butene-2, and cis-butene-2). The enhanced reactivity of cis-butene-2 over trans-butene-2 suggests that a 'wrestling' type collision occurs and that the open side of the cis configuration is sterically favoured over either side of the trans configuration. The effect of a methyl substituent on a sp carbon leads to a 5-fold increase in reactivity (compare methylacetylene with acetylene, but note that two different methods were used in determining the relative reactivities). Allene, when given a statistical factor of ½ for two C=C bonds, is essentially no more reactive than ethylene. The high reactivity of butadiene shows the increase in reactivity when the adduct radical is stabilized by resonance (given a statistical factor of ½ for two C=C bonds, butadiene is about 12 times more reactive than cis-butene-2). Presumably, for butadiene, the increase in reactivity is due to resonance stabilization of the transition-state. Thus, it may be concluded that a substituent either on the reacting carbon or on the adjacent carbon has a distinct effect on reactivity. Moreover, since differences in reactivity have been ascribed to differences in pre-exponential factors, it may be concluded that substitution affects the entropy of activation of CH_3S addition.

These observations are in contrast with the effect of substitution on the addition of CF_3 to olefins(91). Substituents introduced on the carbon adjacent to the reacting carbon were found to exert only minute effects on the pre-exponential factor while substituents on the reacting carbon lead to a 5-fold decrease in the pre-exponential factor; in the latter case the effect was attributed to a loss of internal rotational entropy due to restricted rotation of CF_3 about the incipient C-CF_3 bond. However, methyl substituents located either on the reacting carbon or on the adjacent carbon were found to decrease the activation energy. Moreover, a linear relationship was found between the activation energies and the ionization potentials of the olefins. Surprisingly, butadiene was found to be only 9 times more reactive than ethylene towards CF_3 (see Table 29). This was attributed entirely to a difference in the activation energies, while for CH_3S this was attributed entirely to a difference in the entropies of activation.

This contrasting behaviour suggests that the nature of CH_3S and CF_3 are entirely different, although both radicals are considered to be highly electrophilic. It appears that the stabilization of the transition-state by conjugation or by hyperconjugation is less important for CF_3 than for CH_3S addition. It is possible that the difference in behaviour of CH_3S and CF_3 is due to the larger polarizability of the sulfur atom in CH_3S when compared to the polarizability of the carbon atom in CF_3. However, with the present data, it would be clearly ad hoc to attempt an explanation at this time.

VII CONCLUSION

As a consequence of this study it is hoped that some of the complexity in obtaining rate constants for thiyl radical reactions has been reduced. The present study represents only the beginning. There have been several suggestions throughout this thesis for further experiments. The approaches taken during this study are entirely new and the techniques which were developed appear promising for determining the relative reactivity of all olefins towards thiyl radicals.

APPENDIX 1

DERIVATION OF RATE EQUATIONS

Rate expressions for addition and co-oxidation have been derived from the mechanism given in Figure 2 (page 18). To explain both the isomerization and the addition kinetics, the cis and trans isomers of the olefin are used. The simplification of the kinetics in the absence of oxygen is based on the results of previous workers (22-24). All symbols are defined in Figure 2.

Reaction in the Absence of Oxygen

According to the steady-state approximation for reaction intermediates, X^*, X, and RS, the following relations are available:

$$k_d[M][X^*] = k_3[X] + k_2[X][RSH] \tag{1}$$

$$k_{1c}[RS][C] + k_{1t}[RS][T] = k_d[M][X^*] + k_{-1}[X^*] \tag{2}$$

$$r_i + k_3[X] + k_{-1}[X^*] + k_2[X][RSH] = 2k_4[RS] + k_{1c}[RS][C] + k_{1t}[RS][T] \tag{3}$$

Summation of (1), (2), and (3) leads to,

$$[RS] = \frac{\overline{(r_i^{1/2})}}{(2k_4)^{1/2}} \text{, where } \overline{(r_i^{1/2})} \text{ is the mean square root initiation.} \tag{4}$$

From (2) and (4)

$$[X^*] = \frac{\overline{(r_i^{1/2})}}{(2k_4)^{1/2}} \left[\frac{k_{1c}[C] + k_{1t}[T]}{k_d[M] + k_{-1}}\right] \tag{5}$$

Since above 4 torr, no pressure dependence is observed for isomerization, the collisional de-energization of the excited adduct radical, X*, must be very fast, and hence $k_d[M] >> k_{-1}$.

From (1) and (5)

$$[X] = \frac{k_d[M][X^*]}{k_3 + k_2[RSH]} = \frac{\overline{(r_i^{\frac{1}{2}})}}{(2k_4)^{\frac{1}{2}}}\left[\frac{k_{1c}[C] + k_{1t}[T]}{k_3 + k_2[RSH]}\right] \tag{6}$$

For the initial rate of isomerization when $[C] = [C]_o$ and $[T] = 0$

$$R_{ic} = -\left(\frac{d[C]}{dt}\right)_o = \rho_3 k_3 [X]$$

$$= \frac{\overline{(r_i^{\frac{1}{2}})}}{(2k_4)^{\frac{1}{2}}}\left[\frac{\rho_3 k_3 k_{1c}[C]}{k_3 + k_2[RSH]}\right] \tag{7}$$

Since no order dependence on thiol is observed for the isomerization of butene-2 when $[RSH] < 3 \times 10^{-3}$ mole liter^{-1}, then $k_3 >> k_2[RSH]$.

$$R_{ic} = \frac{\overline{(r_i^{\frac{1}{2}})}}{(2k_4)^{\frac{1}{2}}}\rho_3 k_{1c}[C]$$

Similarly, using equation (6), the rate of addition is

$$R_a = -\left(\frac{d[RSH]}{dt}\right) = k_2[X][RSH]$$

$$= \frac{\overline{(r_i^{\frac{1}{2}})}}{(2k_4)^{\frac{1}{2}}}\left[\frac{k_2[RSH]\left(k_{1c}[C] + k_{1t}[T]\right)}{k_3 + k_2[RSH]}\right] \tag{8}$$

Since rapid isomerization results in an equilibrium concentration of cis and trans olefin during the addition, $k_{1c}[C] + k_{1t}[T]$, may be replaced by $k_1[A]$, where k_1 is the cis-trans equilibrium weighted attack constant which has been defined in reference (24), and where [A] is the total olefin concentration. Then the rate of addition (8) becomes

$$R_a = \frac{\overline{(r_i^{\frac{1}{2}})}}{(2k_4)^{\frac{1}{2}}}\left[\frac{k_1 k_2[RSH][A]}{k_3 + k_2[RSH]}\right]. \tag{9}$$

The rate expression for addition under RS-RS termination, which is given in equation 9, is first order on olefin concentration and half order on initiation. If another termination process was to predominate, then a different order dependence on olefin concentration would be obtained.

Assuming that cross termination predominates;

$$\mathrm{RS} + \mathrm{X} \xrightarrow{k_5} \text{products},$$

then an analogous steady-state derivation to (9) would give,

$$R_a = \frac{\overline{(r_i^{1/2})}}{(2k_5)^{1/2}} \left[\frac{k_1[A]}{k_2[\mathrm{RSH}] + k_3} \right]^{1/2} k_2[\mathrm{RSH}], \qquad (10)$$

in which the dependence on olefin concentration is now half order while the dependence on initiation remains at half order.

Assuming that the mode of termination is,

$$\mathrm{X} + \mathrm{X} \xrightarrow{k_6} \text{products},$$

then an analogous steady-state derivation to (9) would give,

$$R_a = \frac{\overline{(r_i^{1/2})}}{(2k_6)^{1/2}} k_2[\mathrm{RSH}], \qquad (11)$$

in which the rate of addition is independent of olefin concentration while the dependence on initiation remains at half order.

If heterogeneous termination was to predominate, such as

$$\mathrm{RS} + \text{wall} \xrightarrow{k_w'} \text{products}$$

or

$$\mathrm{X} + \text{wall} \xrightarrow{k_w''} \text{products},$$

then the corresponding rate equation for addition would be first order on initiation, rather than the half order dependence obtained for homogeneous terminations.

Reaction in the Presence of Oxygen

In the presence of oxygen, the adduct radical, X, rather than dehydrogenating thiol, reacts with oxygen to form a peroxy radical, XOO, which then dehydrogenates thiol to form a hydroperoxide, XOOH. In this situation, $k_7[O_2] >> k_2[RSH]$, and the term $k_2[RSH]$ may be neglected. Also, because of high pressures, $k_d[M] >> k_{-1}$, and the term containing k_{-1} may be neglected.

Then, applying the steady-state approximation to the intermediates, X*, X, XOO, and RS, the following relations are available:

$$k_{1c}[RS][C] + k_{1t}[RS][T] = k_d[M][X^*] \tag{12}$$

$$k_d[M][X^*] = k_3[X] + k_7[X][O_2] \tag{13}$$

$$k_7[X][O_2] = k_8[XOO][RSH] \tag{14}$$

$$r_i + k_3[X] + k_8[XOO][RSH] = 2k_4[RS]^2 + k_{1c}[RS][C] + k_{1t}[RS][T] \tag{15}$$

Summation of (12), (13), (14), and (15), leads to

$$[RS] = \frac{(\overline{r_i^{1/2}})}{(2k_4)^{1/2}} \tag{16}$$

From (12) and (16)

$$[X^*] = \frac{(\overline{r_i^{1/2}})}{(2k_4)^{1/2}}\left[\frac{k_{1c}[C] + k_{1t}[T]}{k_d[M]}\right] \tag{17}$$

From (13) and (17)

$$[X] = \frac{k_d[M][X^*]}{k_3 + k_7[O_2]}$$

$$= \frac{(\overline{r_i^{1/2}})}{(2k_4)^{1/2}}\left[\frac{k_{1c}[C] + k_{1t}[T]}{k_3 + k_7[O_2]}\right] \tag{18}$$

The initial rate of isomerization of the cis isomer in the presence of oxygen at [T] = 0 is then,

$$R_{1c} = -\left.\frac{d[C]}{dt}\right|_{o} = \rho_3 k_3 [X]$$

$$= \frac{\overline{(r_i^{1/2})}}{(2k_4)^{1/2}} \frac{\rho_3 k_3 k_{1c}[C]}{k_3 + k_7[O_2]} \tag{19}$$

From (14) and (18)

$$[XOO] = \frac{k_7[X][O_2]}{k_8[RSH]}$$

$$= \frac{\overline{(r_i^{1/2})}}{(2k_4)^{1/2}} \left[\frac{k_7[O_2]\left(k_{1c} + k_{1t}[T]\right)}{k_8[RSH]\ k_3 + k_7[O_2]}\right] \tag{20}$$

Then, making use of (20), the rate of co-oxidation is

$$R_0 = -\frac{d[O_2]}{dt} = k_8[XOO][RSH]$$

$$= \frac{\overline{(r_i^{1/2})}}{(2k_4)^{1/2}} \left[\frac{k_7[O_2]\left(k_{1c}[C] + k_{1t}[T]\right)}{k_3 + k_7[O_2]}\right] \tag{21}$$

When rapid isomerization occurs, $k_{1c}[C] + k_{1t}[T]$, may be replaced by $k_1[A]$, where k_1 is the cis-trans equilibrium weighted attack constant and [A] is the total olefin concentration. The rate of co-oxidation is then,

$$R_0 = \frac{\overline{(r_i^{1/2})}}{(2k_4)^{1/2}} \frac{k_1[A]k_7[O_2]}{k_3 + k_7[O_2]} \tag{22}$$

The rate of co-oxidation for olefins without cis-trans isomers is also given by (22), in which case k_1 is the attack constant and [A] is the olefin concentration.

APPENDIX 2

THE RATE EQUATION FOR
THE INHIBITION OF BUTENE-2 ISOMERIZATION BY BUTADIENE-1,3

A relationship for the relative reactivity of cis-butene-2 and butadiene-1,3 towards thiyl radicals can be derived from the following mechanism:

$$\mathrm{RS} + \mathrm{C} \xrightarrow{k_{1c}} \mathrm{X}$$

$$\mathrm{X} \xrightarrow{k_3} \mathrm{C \text{ or } T} + \mathrm{RS}$$

$$\mathrm{RS} + \mathrm{B} \xrightarrow{k_{1b}} \mathrm{Y}$$

$$\begin{matrix}\mathrm{X}\\ \mathrm{Y}\end{matrix} + \mathrm{RSH} \underset{k_2'}{\overset{k_2}{\rightrightarrows}} \mathrm{RS} + \text{products}$$

$$\mathrm{Y} + \text{wall} \xrightarrow{k_w} \text{termination products},$$

where C, T, and B, are cis-butene-2, trans-butene-2, and butadiene, respectively, and where X and Y are the intermediate adduct radicals from C and B, respectively, and where r_i is the rate of initiation.

Then applying the steady-state approximation to the reaction mechanism, the following relations are available:

$$r_i + k_3[X] + k_2[X] + k_2'[Y][RSH] = k_{1c}[C][RS] + k_{1b}[B][RSH] \qquad (1)$$

$$k_{1c}[RS][C] = k_3[X] + k_2[X][RSH] \qquad (2)$$

$$k_{1b}[RS][B] = k_w[Y] + k_2'[Y][RSH] \qquad (3)$$

Summation of (1), (2), and (3), leads to,

$$[Y] = \frac{r_i}{k_w} \tag{4}$$

From (3), and (4), when $[B] = [B]_o$ at $t = 0$,

$$\frac{-d[B]}{dt} = k_2'[RSH][Y] + k_w[Y] = \left[\frac{k_w + k_2'[RSH]}{k_w}\right](r_i)$$

which on integration, assuming that [RSH] is constant, yields

$$[B] = [B]_o - \left[\frac{k_w + k_2'[RSH]}{k_w}\right](r_i)t \ .$$

Then if the inhibition period, t_i, is defined as the time at which $[B] = 0$,

$$r_i\left[\frac{k_w + k_2'[RSH]}{k_w}\right] = \frac{[B]_o}{t_i} \ . \tag{5}$$

Since, $k_3 >> k_2[RSH]$, the rate of isomerization from equation 2 is

$$\frac{-d[C]}{dt} = \rho_3 k_3[X] = \rho_3 k_{1c}[C][RS] \ . \tag{6}$$

From (3)

$$[RS] = \frac{k_w[Y] + k_2'[RSH][Y]}{k_{1b}[B]} = \left[\frac{k_w + k_2'[RSH]}{k_{1b}[B]}\right]\frac{r_i}{k_w}$$

$$= \left[\frac{k_w + k_2'[RSH]}{k_w}\right]\frac{r_i}{k_{1b}[B]} \ . \tag{7}$$

From (6), and (7)

$$\frac{-d[C]}{dt} = \rho_3 k_{1c}[C]\left[\frac{k_w + k_2'[RSH]}{k_w}\right]\frac{r_i}{k_{1b}[B]} \tag{8}$$

Then using (5)

$$\frac{-d[C]}{dt} = \frac{\rho_3 k_{1c}[C]}{k_{1b}[B]}\left(\frac{[B]_o}{t_i}\right)$$

Then the initial rate of isomerization, when $[C] = [C]_o$ and $[B] = [B]_o$, is

$$R_{ic} = -\left(\frac{d[C]}{dt}\right)_o = \rho_3 \frac{k_{1c}}{k_{1b}} \frac{[C]_o}{t_i} . \qquad (9)$$

This rate expression has been derived to explain the butadiene inhibition of cis-butene-2 isomerization as shown in Graph 2. The inhibition periods, obtained from Graph 2, were determined from the points of intersection of the extrapolated initial and final portions of the curves. For each curve, the point of intersection is the time required for all the butadiene to react. Then from the initial rate of isomerization of cis-butene-2 in the presence of butadiene, R_{ic}, and from the inhibition period, t_i, the ratio, $\rho_3 k_{1c}/k_{1b}$, may be determined.

APPENDIX 3

INITIATION FOR A STRONGLY ABSORBING INITIATOR

The rate of initiation throughout the length of a reaction cell will vary considerably when the initiator absorbs light strongly. This becomes more serious in a long reaction cell since uniform diffusion of the intermediate radicals is more difficult. In such cases, the average rate of initiation may be obtained by integrating the local rates of initiation over the cell length. However, when bimolecular termination occurs, the rate of reaction depends on the square root of the initiation rate. In this case, the mean square root initiation may be obtained by integrating the square root of the local rates of initiation over the entire cell length. This may be formulated mathematically for a many-line photolysis source as follows. First the following terms are defined:

I_a is the number of einsteins per second absorbed in a layer $d\ell$ at a depth ℓ from the front face of the cell of length L.

I_0 is the incident light intensity transmitted by the front face,

Φ_λ is the quantum yield of radical production at wavelength λ,

β_λ is the extinction coefficient at wavelength λ, and

α is the initiator concentration.

Now the local rate of initiation is given by

$$r_i(\text{local}) = \sum_\lambda (\Phi I_a)_\lambda = \frac{d}{d\ell}\left[\sum_\lambda (\Phi I_0)(1 - e^{-\beta_\lambda \alpha \ell})\right]$$
$$= \sum_\lambda (\Phi I_0)_\lambda\ \beta_\lambda \alpha e^{-\beta_\lambda \alpha \ell}.$$

The average rate of initiation is given by

$$\overline{r_i} = \frac{1}{L}\int_0^L r_i(\text{local})\ d\ell$$
$$= \frac{1}{L}\int_0^L \sum (\Phi I_0)_\lambda\ \beta_\lambda \alpha e^{-\beta_\lambda \alpha \ell}\ d\ell$$
$$= \frac{1}{L}\sum_\lambda (\Phi I_0)_\lambda (1 - e^{-\beta_\lambda \alpha \ell}).$$

The mean square root initiation is given by

$$\overline{(r_i^{1/2})} = \frac{1}{L}\int_0^L r_i^{1/2}(\text{local})\ d\ell$$
$$= \frac{1}{L}\int_0^L \left[\sum_\lambda (\Phi I_0)_\lambda\ \beta_\lambda \alpha e^{-\beta_\lambda \alpha \ell}\right]^{1/2} d\ell.$$

By defining $G(\alpha,\ell)$ and g as

$$G(\alpha,\ell) = \sum_\lambda \frac{(\Phi I_0)_\lambda\ (\beta_\lambda)}{(\Phi I_0)_1\ (\beta_1)}\ e^{-\beta_\lambda \alpha \ell},$$

where subscript 1 refers to a specific wavelength at 254 mμ,

and $$g = \frac{(\beta_1 \alpha)^{1/2}}{L}\int_0^L G^{1/2}(\alpha,\ell)\ d\ell,$$

then, $\overline{(r_i^{1/2})} = g(\Phi I_0)_1^{1/2}.$ (1)

It has been shown, that under the experimental conditions used here, photolysis of methanethiol is due primarily to absorption of three lines of the mercury arc at 254, 257, and 265 mμ. On this basis the following relation for initiation has been experimentally obtained (22,23):

$$\overline{r_i} = \frac{(\phi I_0)'_{254}}{L}\left[(1-e^{-143.1\alpha\ell}) + 0.51(1-e^{-69.9\alpha\ell}) + 2.95(1-e^{-16.8\alpha\ell})\right] \quad (2)$$

Then by making use of the experimental data in equation 2, g values for various thiol concentrations may be obtained by the numerical integration of $G^{\frac{1}{2}}(\alpha,\ell)$ over the cell length. At low thiol concentrations, when all the exponentials may be expanded, the calculation of g is simplified. For the 10 cm cell,

$$G(\alpha,\ell) = (1 - 143.1\alpha\ell) + 0.252(1 - 69.9\alpha\ell) + 0.346(1 - 16.8\alpha\ell),$$

and $\int_0^{10} G^{\frac{1}{2}}\, d\ell = \int_0^{10} (1.599 - 166.5\alpha\ell)^{\frac{1}{2}}\, d\ell.$

Then, $g = \left(4.79 \times 10^{-3}/\alpha^{\frac{1}{2}}\right)\left[(1.599)^{3/2} - (1.599 - 1665\alpha)^{3/2}\right].$

Table 30 gives calculated g values at various thiol concentrations.

TABLE 30

CALCULATED g VALUES FOR METHYL MERCAPTAN

Methyl Mercaptan Concentration moles liter^{-1}	$\int_0^{10} G^{\frac{1}{2}}\, d\ell$	g
1×10^{-1}	0.7545	0.2854*
5×10^{-2}	1.518	0.4059*
1×10^{-2}	10.073	0.5661*
5×10^{-3}	6.280	0.5310*
1×10^{-3}	4.733	0.3810*
5×10^{-4}	11.181	0.2985*
1×10^{-4}		0.1467
8×10^{-5}		0.1318
5×10^{-5}		0.1048
2×10^{-5}		0.0667
1×10^{-5}		0.0471
5×10^{-6}		0.0323

* Values obtained by numerical integration of $\int_0^{10} G^{\frac{1}{2}}\, d\ell$

To calculate the mean square root initiation, $(\overline{r_i^{1/2}})$, by using equation 1 and the g values of Table 30, it is necessary to calculate $(\Phi I_0)_{254}$ for the unknown set of photolytic conditions. Since $(\Phi I_0)'_{254}$ is known for equation 2, based on hydrogen evolution measurements under a standard set of concentrations of $CH_3SH = 2.15 \times 10^{-4}$ moles liter^{-1} and cis-butene-2 = 5.38×10^{-4} moles liter^{-1}, then $(\Phi I_0)_{254}$ for the unknown conditions can be obtained by comparing the rate of isomerization of the standard blend, R_{ic}, to the rate of isomerization, R'_{ic}, obtained when $(\Phi I_0)'_{254}$ was measured. The relationship used is

$$\frac{(\overline{r_i^{1/2}})'}{(\overline{r_i^{1/2}})} = \frac{R'_{ic}}{R_{ic}} = \frac{(\Phi I_0)'^{1/2}_{254}}{(\Phi I_0)^{1/2}_{254}},$$

and hence $(\Phi I_0)^{1/2}_{254} = 391\ R_{ic}$, where R_{ic} is the rate of isomerization of the standard blend. Then $(\overline{r_i^{1/2}})$ may be calculated for all thiol concentrations from equation 1 and the appropriate g value.

The average rate of initiation, $\overline{r_i}$, may be obtained as well from equation 2 by using the new value of $(\Phi I_0)_{254}$.

An alternative method for obtaining $(\overline{r_i^{1/2}})$ is to use the known rate equation for isomerization (22,23), from which,

$$(\overline{r_i^{1/2}}) = 4.44 \times 10^{-2} \frac{R_{ic}}{[C]},$$

where R_{ic} is the isomerization rate of cis-butene-2 at concentration [C].

APPENDIX 4

OVERALL ACTIVATION ENERGIES FOR ADDITION

Based on the following rate expression for thiol addition to olefins,

$$R_a = \frac{(\overline{r_i^{1/2}})}{(2k_4)^{1/2}} \left[\frac{k_1[A]\ k_2[RSH]}{k_3} \right],$$

activation energies for the rate constant ratio, k_1k_2/k_3, for ethylene, propylene, and butene-2, have been reported to be $(E_1+E_2-E_3) = -5.3$, -7.0, and -11.7 kcal (22,24), respectively. Since E_1 has been shown to be essentially zero (23), the activation energy differences represent E_2-E_3. Then, assuming that E_2 is approximately the same for all olefins, the variation of E_3 with substitution of the olefin is unreasonably large. It appears that the small mercury manometer, which was used to measure rates of addition, was not sufficiently sensitive to measure the very small addition rates which occur at higher temperatures. For this reason the problem was reinvestigated.

The values of $E_1+E_2-E_3$, which are used throughout this thesis, are given in Table 31. They were determined by the method of least squares from the results given in Table 32; the Arrhenius plot is shown in Graph 17.

TABLE 31

OVERALL ACTIVATION ENERGIES FOR ADDITION

Olefin	$(E_1+E_2-E_3)$ kcal
Ethylene	-5.0
Propylene	-5.6
Butene-2	-6.4

TABLE 32

EFFECT OF TEMPERATURE ON THE ADDITION RATE OF VARIOUS OLEFINS

Temperature °K	$1/T \times 10^3$	$R_a \times 10^7$ moles $liter^{-1}$ sec^{-1}	$\log R_a$
Butene-2			
298.2	3.35	3.729	-6.428
309.2	3.23	2.566	-6.591
318.2	3.14	1.870	-6.728
328.2	3.05	1.307	-6.884
339.0	2.95	1.067	-6.972
348.2	2.87	0.784	-7.106
Propylene			
298.2	3.35	8.805	-6.055
308.2	3.24	6.336	-6.198
318.2	3.14	4.601	-6.337
328.2	3.05	3.415	-6.467
338.2	2.96	2.645	-6.578
348.2	2.87	2.356	-6.628
Ethylene			
298.2	3.35	4.155	-6.382
308.2	3.24	3.195	-6.496
318.2	3.14	2.501	-6.602
328.2	3.05	1.894	-6.723
338.2	2.96	1.552	-6.809
348.2	2.87	1.225	-6.912

$[A] = 5.38 \times 10^{-3}$ moles $liter^{-1}$ = Olefin concentrations

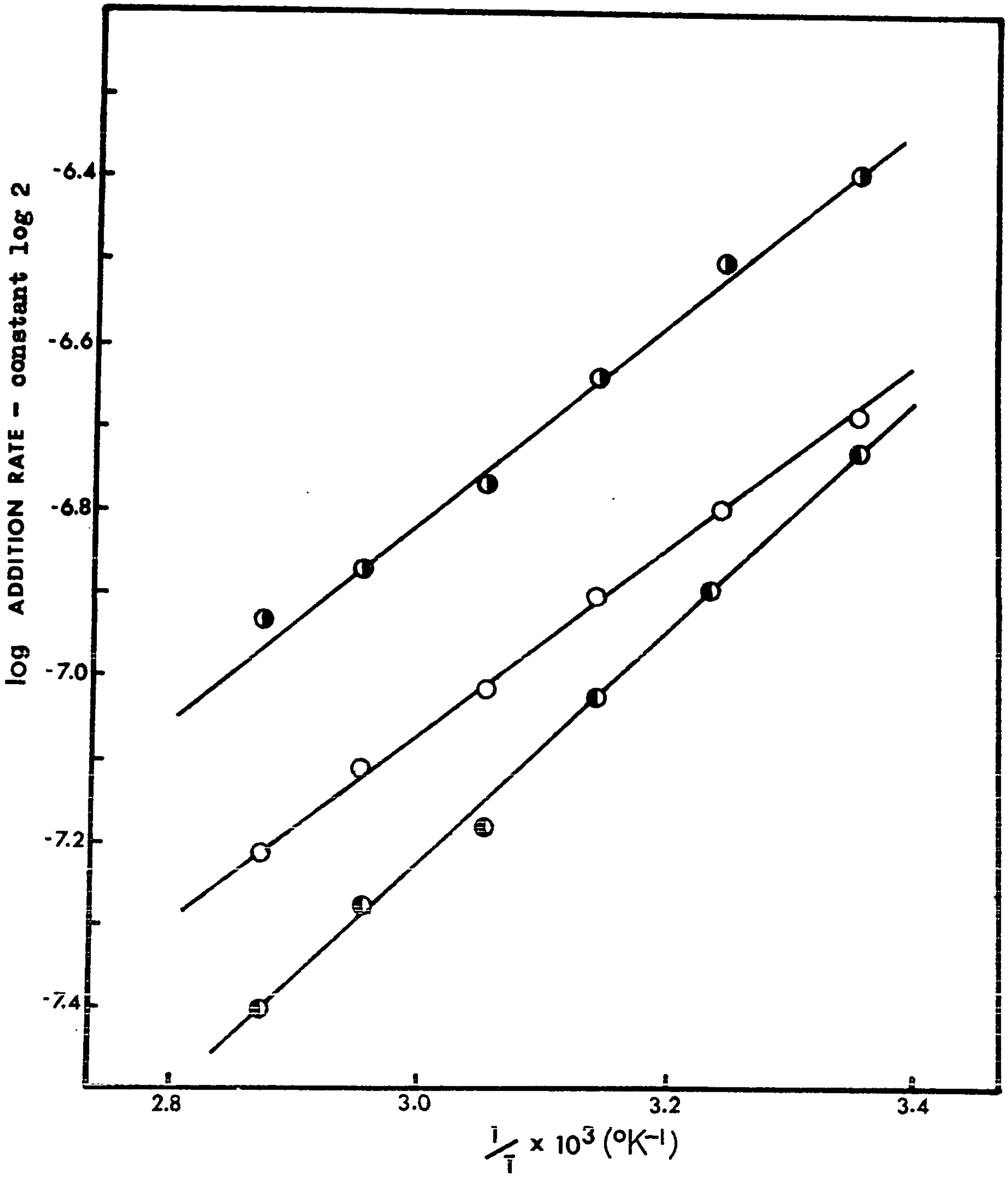
$[CH_3SH] = 5.38 \times 10^{-3}$ moles $liter^{-1}$

Reaction Cell Length = 2 cm.

GRAPH 17

ARRHENIUS PLOTS FOR ADDITION TO VARIOUS OLEFINS

○ ETHYLENE
◐ PROPYLENE
◑ CIS BUTENE-2



APPENDIX 5

CO-OXIDATION UNDER HETEROGENEOUS TERMINATION

Table 33 contains the rates of co-oxidation of several olefins at 25°C which were not important in the evaluation of rate constants; these results are complimentary to those of Table 18 which shows that initiation is first order for co-oxidation. In each case the rate of co-oxidation, R_0, represents the total pressure change, $-dP/dt$, expressed in moles liter^{-1} sec^{-1}.

TABLE 33

CO-OXIDATION RATES AT 25°C

Oxygen Concentration x 10^3 moles ℓ^{-1}	R_0 x 10^8 no filter moles ℓ^{-1} sec^{-1}	R_0 x 10^8 26.6% T filter moles ℓ^{-1} sec^{-1}	Order Dependence on Initiation
[Ethylene] = 10.76 x 10^{-3} moles liter^{-1}			
0.00	10.3	—	—
0.05	8.92	—	—
0.17	7.88	—	—
0.68	7.02	—	—
1.35	6.32	—	—
2.69	5.00	—	—
5.38	4.94	—	—
21.51	3.28	—	—
[CH_3SH] = 1.08 x 10^{-3} moles liter^{-1}(10 cm cell)			

……

TABLE 33 (continued)

Oxygen Concentration $\times 10^3$ moles ℓ^{-1}	$R_0 \times 10^8$ no filter moles ℓ^{-1} sec^{-1}	$R_0 \times 10^8$ 26.6% T filter moles ℓ^{-1} sec^{-1}	Order Dependence on Initiation
[Propylene] = 2.69×10^{-3} moles liter^{-1}			
0.00	21.4	10.7	0.52
0.15	23.3	—	—
0.54	31.3	7.30	0.96
2.69	23.3	5.66	0.97
5.83	17.8	—	—
$[CH_3SH] = 10.76 \times 10^{-3}$ moles liter^{-1}(10 cm cell)			
[Butene-2] = 2.69×10^{-3} moles liter^{-1}			
0.00	6.70	—	—
0.54	13.3	—	—
1.35	13.0	—	—
2.69	14.1	—	—
5.38	12.0	—	—
10.8	10.1	—	—
16.1	7.52	—	—
$[CH_3SH] = 2.69 \times 10^{-3}$ moles liter^{-1}(10 cm cell)			
[Butadiene-1,3] = 1.08×10^{-3}moles liter^{-1}			
0.00	18.8	4.96	1.01
0.06	41.7	13.5	0.85
0.27	42.9	13.5	0.86
1.08	41.9	11.8	0.96
2.69	42.5	15.7	0.73
5.38	42.8	14.8	0.80
$[CH_3SH] = 10.76 \times 10^{-3}$ moles liter^{-1}(10 cm cell)			

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