

THE CHARACTERISATION OF OXIDE CATALYSTS

BY INVESTIGATIONS ON

EXCHANGE REACTIONS.

BY

JAMES REDPATH CHRISTIE B.Sc.

Thesis presented for the degree of

DOCTOR OF PHILOSOPHY

UNIVERSITY OF EDINBURGH

OCTOBER, 1972.



Abstract

The catalytic oxidation of propylene to form acrolein, over a range of tin-antimony-oxide catalysts, has been investigated by a number of physical techniques including isotopic exchange and oxidation. Propylene oxidation reactions and exchange reactions of propylene/D₂O, isobutene/D₂O and ¹⁶O₂ / ¹⁸O₂, over the catalysts, have been studied in a static system. The results of a kinetic study at reaction temperatures between 373 and 873 K are reported and possible reaction mechanisms are discussed.

The propylene/D₂O exchange reaction and the propylene oxidation reaction both occur via a common, symmetrical intermediate. It is proposed that the rate determining step is the abstraction of an allylic hydrogen atom, from the propylene molecule, to form the allylic intermediate. The isobutene/D₂O exchange reaction most probably proceeds via a tertiary carbonium ion intermediate. It is suggested that isotopic oxygen exchange proceeds via a dissociative atomic mechanism.

Catalytic activity is shown to be greatest at low atom % antimony compositions. It is proposed that the formation of a tin oxide-antimony oxide solid solution may be responsible for the observed enhanced activity. The moderating influence of the Sb₂O₄ matrix is, however, responsible for catalyst selectivity.

Contents

Part I

General Introduction

<u>Chapter 1</u>	<u>Introduction to Catalysis</u>	<u>Page</u>
1.1	Definition	1
1.2	Historical Background	1
1.3	Heterogeneous Catalysis	2
1.4	Adsorption	3
1.5	Mechanism of Heterogeneous Catalysis	5
1.6	Catalytic Activity	7
1.7	Metal Oxide Catalysts	8
1.8	Object of the Present Investigation	10
<u>Chapter 2</u>	<u>Exchange Reactions</u>	
2.1	Introduction	12
2.2	Analysis of the Mass Spectral Data	13
2.3	Computer Programme	16
2.4	Final Equilibrium of an Exchange Reaction	16
2.5	Determination of Rate Constants	18
2.6	Arrhenius Plots	20
2.7	Kinetics	21

2.8	Classification and Possible Mechanisms of Exchange Reactions	21
2.9	Isotopic Oxygen Exchange	24
<u>Chapter 3</u>	<u>Oxidation Reactions</u>	
3.1	Introduction	25
3.2	Catalytic Oxidation of Propylene	25
3.3	Mechanisms of Propylene Oxidation	26
3.4	The Acrylonitrile Process	31

Part II

Experimental and Results

<u>Chapter 4</u>	<u>Experimental Apparatus and Techniques</u>	
4.1	Introduction	33
4.2	Gas Handling System	33
4.3	Reaction Vessel and Capillary Leak	34
4.4	The Mass Spectrometer	36
4.5	Volume Calibrations	38
4.6	Materials	39
4.7	Catalyst Preparation	39
4.8	Infrared Spectroscopy	42

<u>Chapter 5</u>	<u>Exchange Reactions of Unsaturated Hydrocarbons with Heavy Water</u>	<u>Page</u>
5.1	Introduction	43
5.2	Experimental	44
5.3	Results	
5.3.1	Propylene/D ₂ O Exchange	45
5.3.2	Heavy Water Pretreatment	50
5.3.3	Catalytic Activity in Relation to Catalyst Composition	52
5.3.4	Isobutene/D ₂ O Exchange	55
5.3.5	Infrared Spectroscopic Analysis of Reaction Products	61
<u>Chapter 6</u>	<u>Propylene Oxidation Reactions</u>	
6.1	Introduction	64
6.2	Experimental	64
6.3	Results	66
6.4	Investigation of Propylene/ ¹⁶ O ₂ Oxidation by a Flow System Technique	
6.4.1	Introduction	74
6.4.2	Experimental	74
6.4.3	Results	75

<u>Chapter 7</u>	<u>Isotopic Oxygen Exchange between the Gas Phase and the Solid Catalyst</u>	<u>Page</u>
7.1	Introduction	78
7.2	Kinetics	79
7.3	Mechanisms	84
7.4	Experimental	85
7.5	Results	86

Part III

Discussion and Conclusion

<u>Chapter 8</u>		
	Discussion	90
	Conclusion	108
	Appendix	110
	References	114

PART I

GENERAL INTRODUCTION

CHAPTER I

Introduction to Catalysis.

1.1. Definition.

A catalyst is a substance that increases the rate at which a chemical reaction reaches equilibrium, without itself undergoing chemical change.

The equilibrium position so attained must be the same as that observed in the absence of the catalyst. Consequently a catalyst must affect equally the rates of both forward and reverse reactions. A catalyst can increase the rate of only those processes that are thermodynamically favourable, it cannot initiate reactions that are not so favoured.

Catalysed reactions may be divided into two main groups:-

(1) Homogeneous catalysis, where both the catalyst and the reactants are in the same phase.

(2) Heterogeneous catalysis, where the catalytic reaction takes place at an interface between two phases.

This thesis is concerned only with heterogeneous catalytic reactions occurring at interfaces between solids and gases.

1.2. Historical Background.

The concept of catalysis was first introduced to the world of science in 1835 when Berzelius⁽¹⁾ reviewed a number of isolated observations made by, among others, Van Marum⁽²⁾, Kirchoff⁽³⁾,

Thenard⁽⁴⁾, Davy⁽⁵⁾, Dobereiner⁽⁶⁾ and Mitscherlich⁽⁷⁾ and proposed the existence of "a catalytic force". Berzelius considered only the amounts of the products formed by the catalyst and not their rate of formation. A more comprehensive understanding of catalysis was introduced by Ostwald⁽⁸⁾ in 1902, when he proposed that the rate of a reaction could be taken as a measure of catalytic activity. He defined a catalyst as, "any substance which alters the velocity of a chemical reaction without appearing in the end products". By correlating catalytic activity with a measurable quantity he laid the foundations upon which modern ideas of catalysis are based.

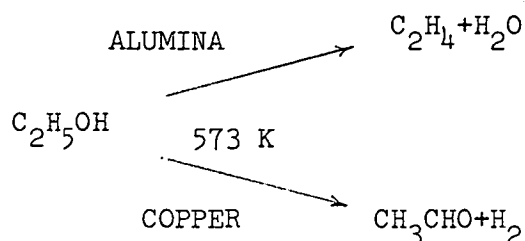
1.3. Heterogeneous Catalysis.

Heterogeneous catalytic reactions occur when the rate of a chemical reaction is increased by the presence of an interface between two phases. As the results of many experimental investigations began to accumulate so a number of theories explaining the action of heterogeneous catalysts were proposed.

One such theory of the nineteenth century proposed that the reactants formed an intermediate compound with the bulk solid. The intermediate then either decomposed or reacted further to produce the observed products. Although changes in the catalyst surface were occasionally observed during the course of some reactions, direct evidence for the existence of these intermediates was lacking. Thus, the intermediate compound theory did not gain wide acceptance.

A further theory based on "contact action" was proposed by Faraday⁽⁹⁾, whereby increased rates of reaction were brought about by physical forces of attraction between the catalyst and the

reactants. The increased rate of reaction was due to the enhanced concentration of reactants close to the surface of the solid. The high specificity of catalytic action, take for example ethanol:-



tends to rule out Faraday's theory.

Specificity considerations prompted Sabatier⁽¹⁰⁾, to postulate the existence of unstable surface compounds as intermediates in heterogeneous catalysis. Sabatier's theory was further supported by Langmuir's⁽¹¹⁾ work on adsorption, which indicated that metal surfaces adsorbed gases and that, invariably, the amount of adsorption increased with pressure to a constant maximum. Consequently he proposed that the adsorbed molecules were held to the surface by essentially chemical bonds and that, the amount of adsorption depended on the number of surface sites available for bonding.

1.4. Adsorption.

It has been clearly shown that catalytic reactions involve the adsorption of at least one of the reactants upon the catalyst surface. Adsorption takes place with a decrease in surface free energy and in entropy, thus, it is generally exothermic. Although the strength of adsorption together with the extent of adsorption may vary widely from system to system, it is possible to distinguish between two kinds

of adsorption, namely physical adsorption and chemisorption.

Physical Adsorption.

Under the appropriate conditions physical adsorption can occur between all gases and all solids and as no chemical bonds are formed the forces involved are weak and of the type which give rise to the cohesive properties of liquids, that is van der Waals forces⁽¹²⁾. The heat of physical adsorption is generally low, similar in magnitude to the heat of condensation of the gas being adsorbed. Provided the surface is readily accessible then the rates of adsorption and desorption are rapid as no activation energy is required, and the process is readily reversible.

Physical adsorption though not catalytically important except in very special cases⁽¹³⁾ can be useful for the measurement of surface properties such as surface areas⁽¹⁴⁾ and pore size distributions^(15,16).

Chemisorption.

The process of chemisorption⁽¹⁷⁾ involves the rearrangement of the electrons of the interacting gas and solid, with the consequential formation of chemical bonds. Generally speaking heats of chemisorption are much higher than those of physical adsorption, values of $\approx 100-200$ kJ. mol⁻¹ are frequently found and thus rates of desorption are usually low. Consequently one would expect that chemisorption would involve a considerable activation energy, this is in fact usually so, however, under very special conditions the activation energy may effectively approach zero⁽¹⁸⁾.

Since the adsorbate must make direct contact with the surface, chemisorption is always confined to a single atomic or molecular layer

and is specific in nature. It is now generally accepted that chemisorbed species act as intermediates in heterogeneous catalytic reactions. Consequently a considerable effort has been made in order to ascertain the nature and properties of the adsorbed species. A wide range of experimental techniques including I.R., E.S.R., L.E.E.D. and X-RAY, (19,20, 21,22) have been brought to bear on this problem. Their findings indicate that the adsorbed gas may be present on the surface in a variety of species, often with considerable rearrangement of the molecule, and that the presence of another gas can markedly affect the relative proportions of these species. The more important aspects of chemisorption have been discussed in a review by Gundry and Tompkins⁽¹⁹⁾.

To achieve efficient catalysis, the strength of adsorption is important. If a reactant is too strongly adsorbed on the surface it will be difficult to remove and may constitute a poison, while a weakly adsorbed reactant may not remain on the surface long enough to react.

1.5. Mechanism of Heterogeneous Catalysis.

A catalytic reaction which takes place on a surface can be broken down into five consecutive steps.

1. Diffusion of the reactant molecules to the surface.
2. Chemisorption of at least one of the reactant species on the surface.
3. Reaction of these adsorbed species either among themselves, with physically adsorbed species or with other molecules colliding with the surface.

4. Desorption of the products.
5. Diffusion of the products away from the surface.

In principle it is possible that any of the above steps may be rate determining. However, in practice as diffusion in the gaseous state requires no activation energy, then steps 1 and 5 are unlikely to be rate determining, except in the case of highly porous catalysts.

The actual rate determining step may be found by a careful analysis of kinetic data, preferably coupled with spectroscopic information on the adsorbed species. A typical approach was that of Kummer and Emmett⁽²³⁾ who found that the rate of exchange of $^{28}\text{N}_2$ with $^{30}\text{N}_2$ was in good agreement with the rate of formation of ammonia from nitrogen and hydrogen, thus concluding that the chemisorption of nitrogen was the rate determining step.

There are two well established mechanisms which explain the combination of reactants at a catalyst surface, namely, the Langmuir - Hinshelwood^(24,25) and Eley - Rideal^(26,27) mechanisms. The Langmuir - Hinshelwood mechanism assumes that equilibrium is established between the gaseous reactants and the adsorbed surface species and that reaction takes place between the adjacent chemisorbed species. The rate determining step is assumed to be the reaction between the adsorbed molecules.

The Eley - Rideal mechanism postulates that only one of the reactant species is chemisorbed to the surface and that reaction occurs between a chemisorbed molecule and a physically adsorbed molecule. This

mechanism was proposed as a result of work carried out on low temperature hydrogen-deuterium exchange⁽¹⁸⁾. Although detailed arguments have been put forward in support of each of these mechanisms, in the case of hydrogen-deuterium exchange there is no clear evidence that one of these mechanisms operates to the total exclusion of the other.

The kinetics of surface reactions are determined by the concentrations of adsorbed species, thus, gas phase analysis is an indirect method of studying the nature of chemisorbed species and surface reactions. However, much valuable information can be obtained by the use of deuterium or other tracer elements^(28,29,30,31 and 32). A more direct approach involves the use of various forms of spectroscopy^(33,20,34), to study the nature of the stable species adsorbed on the catalyst surface.

1.6. Catalytic Activity.

Over the years many attempts have been made to correlate catalytic activity with various properties of the catalyst, however, there is still no single theory capable of interpreting and predicting the action and activity of all types of catalysts.

The "geometric factor" which embodies such considerations as lattice spacing and surface structure has been extensively investigated. Reviews by Bond and Wells⁽³⁵⁾ and by Siegel⁽³⁶⁾, based on the relationship between stereochemical considerations and the mechanism

of olefin hydrogenation, indicate that catalytic activity may be favoured if the reacting species interacts with the surface in such a way that its atoms attain a particularly good fit, relative to the array of atoms in the solid surface.

The factors which determine the relationship between catalytic activity and the electronic structure of the bulk solid, can be collectively termed "the electronic factor"⁽³⁷⁾. It is now generally accepted that, for most reactions, transition metals have a greater activity than non-transition metals, due to the vacant d-orbitals of the former⁽³⁸⁾. Correlation between the structure of the d-band and catalytic activity has been obtained by the use of alloys which allow a continual variation of d-band character^(39,40).

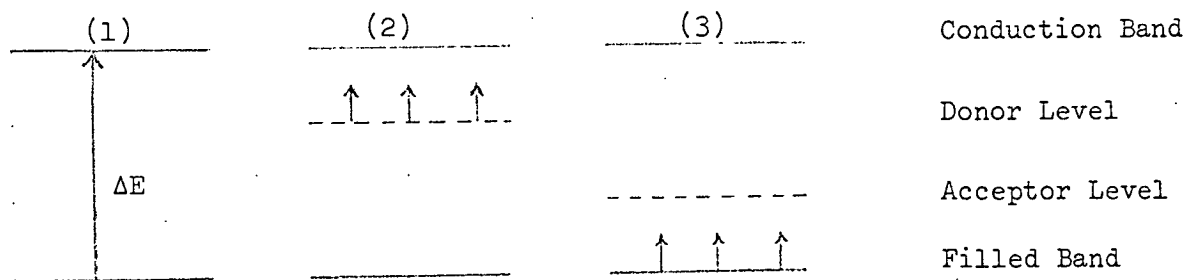
With regard to metal oxide systems, the current trend to use mixed oxide catalysts makes a significant appraisal of the electronic factors extremely complex. A molecular orbital or crystal field approach to the interaction between the chemisorbed species and the surface, would appear to yield the most complete picture.

1.7. Metal Oxide Catalysts.

Since the development of the electron theory of catalysis there have been two main schools of thought, one has asserted that partially filled d-orbitals are important, while the other has proposed that semi-conductivity is the principle factor. By considering the change in crystal field stabilisation energy which occurs during the formation and breakdown of surface complexes, Dowden and Wells⁽⁴¹⁾, have used the

concepts of crystal field theory to explain certain activity patterns observed in a series of transition metal compounds.

If the molecular orbital theory is applied to electrons in semiconductors, then we obtain a separation of the energy states of free electrons into bands which may overlap or be separated by a forbidden energy gap of width ΔE ⁽⁴²⁾. Semiconductors then possess a filled band of valency electrons, separated from a conduction band to which electrons can be promoted if they possess the energy to overcome ΔE . If the energy gap ΔE is too large for electron promotion to be feasible, then the material is said to be an insulator. Band theory proposes these types of semiconductors:-



- (1) Insulator or intrinsic conductor.
- (2) n-type conductor.
- (3) p-type conductor.

In n-type conductors, the impurity levels are situated just below the conduction band and conduction is by means of electrons promoted to the conduction band.

In p-type conductors the impurity ^{levels}~~atoms~~ are located near the filled band and abstract electrons from the filled band so leaving empty states, thus conduction is by means of positive holes in the filled band. Semiconductivity in oxides may result from

non-stoichiometry which can be caused by either vacant lattice sites or by suitable doping of the catalyst. The subject of semiconductivity in oxides has been extensively reviewed by Stone⁽³⁷⁾, Hauffe⁽⁴³⁾ and Fensham⁽⁴⁴⁾.

The subject of semiconductivity and catalysis revolves around the boundary layer theory, the d-electron configuration theory and the crystal field theory, all of which have been extensively discussed. (45, 46 and 41) However, no single theory is capable of interpreting and predicting the action and activity of all metal oxide catalysts.

An attempt has been made to classify heterogeneous catalysts by their electrical conductivity⁽²⁸⁾. Thus, metal oxides classed as semiconductors are catalytically active for oxidation, reduction, dehydrogenation, cyclisation and hydrogenation. Insulators, acid site catalysts, are catalytically active for cracking, isomerisation, polymerisation, dehydration, alkylation, hydrogen transfer, halogenation and dehalogenation.

1.8. Object of the Present Investigation.

In recent years metal oxides have assumed major importance as catalysts for the oxidation of olefins to produce valuable raw materials for the polymers and plastics industry. Thus, propylene can be oxidised with air to give acrolein by the use of cuprous oxide^(47,48), bismuth-molybdenum-oxide mixtures^(49,50,51) or tin-antimony-oxide mixtures⁽⁵²⁾ as catalysts. If the oxidation is carried out with an air-ammonia mixture then the product from propylene is acrylonitrile^(53,50), while from butene-1 oxidative dehydrogenation yields

butadiene^(54,55). In view of the industrial importance of such oxidation products, it is desirable that the factors responsible for both the activity and selectivity of the catalysts should be clarified, and that the reaction mechanisms involved should be known.

This investigation is concerned with the catalytic oxidation of propylene to form acrolein using a range of tin-antimony-oxide mixtures as catalysts. The object being to obtain a better understanding of the overall acrylonitrile process, and if possible, provide some correlation with the properties of the catalysts. It seems likely that the initial step in the reaction involves dissociative chemisorption of propylene to form an allyl type of intermediate, which then loses further hydrogen before taking up oxygen from the catalyst to produce acrolein. Clarification of the initial "hydrogen" step is being attempted by a study of the exchange reaction between propylene and deuterium oxide. The oxygen stage of the process is being investigated by a study of the isotopic oxygen exchange reaction, combined with an attempt to determine the mode of oxygen atom incorporation into the oxygen containing products by the catalytic oxidation of propylene in the presence of $^{18}\text{O}_2$.

CHAPTER 2

Exchange Reactions.

2.1. Introduction.

For satisfactory quantitative mass spectrometric analysis of chemical mixtures it is essential that the following conditions, described by Beynon⁽⁵⁶⁾, be satisfied:-

- (1) The mass spectrum of any component must not be affected by the presence of another component.
- (2) The mass spectrum of a mixture must be a linear superposition of the spectra of the various components.
- (3) The ion beam intensity for any component must be proportional to the partial pressure of that component in the reaction vessel.
- (4) The characteristic mass spectrum of any particular molecule must remain stable for a considerable period of time.
- (5) The sensitivity of the mass spectrometer must remain reasonably constant.
- (6) For exchange reactions the above parameters must be independent of the weight of the molecule.

Conditions 1, 2 and 3 have been verified by previous workers. Conditions 4 and 5 were shown to be satisfied by experimental reproducibility of the mass spectra. Condition 6 is dependent on parameters such as the extent of fragmentation and may vary for non exchanged and fully exchanged species.

2.2. Analysis of the Mass Spectral Data.

The mass spectrometric analysis of an exchange reaction yields data in the form of "raw peak heights" which cannot be used directly to compute the percentages of the isotopic species. Various corrections must be applied to the mass spectral data to account for background in the mass spectrometer, the occurrence of natural isotopes and fragmentation of the molecules. The corrections were applied to the data in the following order.

I Background Corrections:-

Background in the mass spectrometer was due to two factors:-

- (1) Residual gas in the mass spectrometer ion chamber.
- (2) Inherent background.

The residual gas background spectrum was produced by ionisation of the air molecules and water vapour always present in the ion chamber. Desorption of hydrocarbons from the walls of the ion chamber could be brought about by admission of the reaction mixture; this produced the inherent background spectrum.

It was, therefore, necessary to record the total background spectrum immediately prior to the start of a run and at the end of the run. The two background scans were then averaged and subtracted from the peaks to which they contributed in the hydrocarbon mass spectrum. Smooth curves were then drawn through the points corresponding to the various masses, to give an accurate graph of peak height against time. In general the background was found to be negligible.

II Isotope Corrections:-

Naturally occurring carbon and hydrogen contain 1.081% ^{13}C and 0.016% D respectively, thus, the mass spectra of hydrocarbons contain peaks at mass numbers higher than those of the parent molecules. The contribution from these isotopes must be taken into account and can be measured either experimentally or by calculation. Since the ratios of the isotopes are constant throughout the range of naturally occurring hydrocarbons, then for any hydrocarbon C_nH_m of mass M the peak heights at M+1, M+2, etc. may be calculated relative to the peak height PM at mass M by using the isotopic abundances given above. For a hydrocarbon C_nH_m :-

$$100 \frac{\text{PM}+1}{\text{PM}} = \left\{ n \left(\frac{1.081}{98.919} \right) + m \left(\frac{0.016}{99.984} \right) \right\} 100$$

and

$$100 \frac{\text{PM}+2}{\text{PM}} = \left\{ n \frac{(n-1)}{2} \left(\frac{1.081}{98.919} \right)^2 + m \frac{(m-1)}{2} \left(\frac{0.016}{99.984} \right)^2 \right\} 100$$

The values of these factors will vary with the isotopic content of the molecules since replacement of H by D diminishes the contributions of naturally occurring D. Thus, for the species $\text{C}_n\text{H}_{m-x}\text{D}_x$ the values of the corrections are obtained by substituting m-x for m in the above equations.

Isotopic corrections were carried out in a systematic manner starting with the lowest masses and working upwards to the higher masses using the corrected values at every mass to calculate the contributions to the higher masses.

III Fragmentation Corrections:-

Molecules entering the ion source region of the mass spectrometer are subjected to impact by electrons from the filament. If the electron transfers sufficient energy to the molecule to exceed its ionisation potential then positive ions may be produced in accordance with the Franck-Condon Principle, e.g. for a hydrocarbon C_nH_m we have $C_nH_m + e^- \rightarrow C_nH_m^+ + 2e^-$. Further dissociation of the molecule by breakage of the carbon-hydrogen bonds may result from impact with higher energy electrons, e.g. $C_nH_m + e^- \rightarrow C_nH_{m-x}^+ + xH + 2e^-$.

A hydrocarbon molecule of mass M will, therefore, exhibit peaks at M-1, M-2, M-3, etc. Thus, in order to determine the isotopic content of the partially exchanged hydrocarbon molecules the contributions of these isotopic fragments to isotopes at lower masses must be taken into account. The contributions were minimised by operating the mass spectrometer at low electron voltages. However, because the sensitivity decreased with decreasing electron energy, a compromise had to be reached between sensitivity and extent of fragmentation. For the heavy water exchange work described in this thesis a value of between 10 and 20 eV was found to be perfectly satisfactory.

The fragmentation or cracking patterns of both the non-deuterated and fully deuterated hydrocarbons used in this work were found to be very similar. Therefore, the assumption that the cracking pattern was independent of either the isotopic substitution or the position of isotopic substitution in the molecule was justified. The fragmentation corrections could then be calculated on a statistical basis from the fragmentation pattern of the light

hydrocarbon, determined before each experiment. However, for certain hydrocarbon molecules it is known that hydrogen is lost more readily and deuterium less readily than statistical calculations, based on the fragmentation pattern of the light compound, predict. Thus, a computer programme, which interpolated between light and heavy fragmentation patterns, was used to calculate the actual fragmentation corrections. These values were then found to be in excellent agreement with the fragmentation corrections obtained on a purely statistical basis. Therefore, for the work in this thesis fragmentation corrections, based on a purely statistical programme, were found to be perfectly satisfactory. The fragmentation corrections were carried out by a process similar to that used for the isotopic corrections, but starting instead with the highest mass and working systematically down to the lowest mass.

2.3. Computer Programme for the Statistical Analysis of the Mass Spectral Data.

The mass spectral data for the hydrocarbons was, firstly, corrected for naturally occurring isotopes, then corrected for fragmentation on a statistical basis by means of the computer programme shown in Appendix I.

An example of fragmentation correction, calculated by hand on a statistical basis, is given by Jagers⁽⁵⁷⁾.

2.4. Final Equilibrium of an Exchange Reaction.

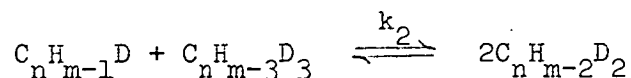
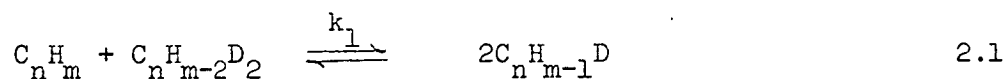
Two kinds of equilibria will be established at equilibrium in the exchange reaction between a hydrocarbon C_nH_m and D_2 or D_2O :-

(1) An equilibrium distribution between the total amount of deuterium in the "hydrocarbon" and the total amount of deuterium in the "hydrogen".

(2) An equilibrium between the relative amounts of the different isotopic species of hydrocarbons present.

Experimentally it is found that the distribution of deuterium between the "hydrocarbon" and the "hydrogen" usually differs slightly from the value expected in terms of a random distribution, the amount of deuterium in the hydrocarbon usually being greater than that calculated statistically. This is due to the fact that the carbon-deuterium and carbon-hydrogen bonds do not have the same bond strengths, the deuterium preferring to be incorporated into the "hydrocarbon" rather than into the "hydrogen".

Values obtained for the second type of equilibrium are fairly close to those expected for a random distribution of the hydrogen or deuterium atoms between the various isotopic species of the hydrocarbon. Therefore, the values of the equilibrium constants for the reactions



etc.

can be calculated from a combination of terms in the appropriate binomial expansion and may be expressed in general terms as:-

$$k_i = \frac{\binom{i}{m}^2}{\binom{i-1}{m} \binom{i+1}{m}} \quad 2.2$$

where the symbol $\binom{i}{m}$ represents the number of ways of selecting i objects from a group of m identical objects. The interconversion equilibrium constants calculated in this way were in good agreement with those derived experimentally.

2.5. Determination of Rate Constants.

The rate of an exchange reaction may be calculated by two methods depending on either the rate of incorporation of deuterium into the hydrocarbon or the rate of disappearance of the parent hydrocarbon. In the former case the rate can be determined from the parameter ϕ , defined by:-

$$\phi = \sum i d_i \quad 2.3$$

where d_i is the percentage of isotopic species containing i deuterium atoms at time t . Provided all the hydrogen atoms in the hydrocarbon molecule are equally susceptible to exchange and provided that the influence of isotopes on the rate of reaction is ignored, the course of the exchange reaction will be given by the first order equation:-

$$\frac{d\phi}{dt} = k\phi \left(1 - \frac{\phi}{\phi_\infty}\right) \quad 2.4.$$

where $k\phi$ is the rate constant equivalent to the number of deuterium atoms entering 100 molecules of hydrocarbon in unit time at the start

of the reaction and ϕ_{∞} is the equilibrium value of ϕ , which may be calculated or obtained experimentally.

Integration of equation (4) yields the first order equation:-

$$-\log_{10}(\phi_{\infty} - \phi) = \frac{k\phi t}{2.303 \phi_{\infty}} \quad -\log_{10}(\phi_{\infty} - \phi_0) \quad 2.5$$

Although equations 2.4 and 2.5 are only approximately true because of the assumption that all isotopic species react at the same rate, they are found to be obeyed in a wide variety of exchange reactions. Failure to obey equation 2.5 may indicate differences in reactivity between the different hydrogen atoms in the hydrocarbon or poisoning of the catalyst.

The rate of disappearance of the light hydrocarbon is given by the empirical first order equation:-

$$-\log(d_0 - d_{\infty}) = \frac{k_0 t}{2.303(100 - d_{\infty})} \quad -\log(100 - d_{\infty}) \quad 2.6$$

where d_0 is the percentage of the light hydrocarbon at time t and 100 and d_{∞} are the initial and final percentages of this species respectively. If the ratio of deuterium to hydrocarbon used is large, then d_{∞} will be negligible and equation 2.6 simplifies to:-

$$-\log d_0 = \frac{k_0 t}{230.3} - 2 \quad 2.7$$

The ratio of the two rate constants in equations 2.5 and 2.6 known as the "M value" is defined as:-

$$M = \frac{k\phi}{k_0} \quad 2.8$$

and represents the mean number of hydrogen atoms replaced by deuterium atoms in each molecule of the hydrocarbon undergoing exchange in the initial stages of the reaction.

2.6. Arrhenius Plots.

The calculation of isotopic distributions at particular times and temperatures provided the necessary data to plot $\log(\phi_{\infty} - \phi)$ and $\log(d_0 - d_{\infty})$ against time according to equations 2.5 and 2.6. From the slopes of the resultant lines, which should be straight for non-poisoned or non-accelerating reactions, the initial rates of reaction were obtained and the M value of the reaction calculated.

By use of the Arrhenius equation

$$k = Ae^{-\frac{E}{RT}}$$

$$\text{or } \log_{10} k = \log_{10} A - \frac{E}{2.303RT}$$

where k = rate constant.

A = frequency factor.

E = apparent activation energy (kJ mole^{-1}).

R = gas constant ($\text{in kJ K}^{-1} \text{ mole}^{-1}$).

T = temperature in K.

then values of E and $\log_{10} A$ may be estimated from plots of $\log_{10} k$ Vs $\frac{K}{T}$. E was expressed in kJ mole^{-1} and in $\log_{10} A$, A in $\text{mol sec}^{-1} \text{ m}^{-2}$. The latter value being calculated from the number of molecules of reactant in the reaction vessel and the surface area of the catalyst.

2.7. Kinetics.

The rate constants $k\phi$ and k_0 are constant only for the course of an exchange reaction with a single mixture of reacting gases. They are pressure dependent and vary as the relative pressures of the gases in the reaction mixture are altered. Thus, the true pressure dependencies of the reaction can only be determined by carrying out the reaction with a series of different reaction mixtures.

The reason for the apparent first order kinetic behaviour of an exchange reaction can be seen from a consideration of the processes occurring during the reaction. On admission of the reaction mixture to the catalyst, two things happen:-

(1) The surface concentrations of the adsorbed species build up to their equilibrium values and thereafter remain constant.

(2) The exchange reaction commences and eventually leads to equilibrium between all the species in the system.

Process (1) will be rapid but (2) cannot go to completion until all the gas phase has been adsorbed and desorbed and hence throughout most of the time required for the exchange reaction there will be equilibrium concentrations of the different types of adsorbed species. The only factor which reduces the rate of exchange from its initial value is the approach of the isotopic content of the "hydrogen" and "hydrocarbon" to their equilibrium values and this leads to the apparent first order behaviour.

2.8. Classification and Possible Mechanisms of Exchange Reactions.

Exchange reactions of hydrocarbons with deuterium or D_2O can be divided into two main categories, namely those in which hydrogen

is replaced by deuterium in a simple or stepwise fashion and those involving multiple exchange.

Simple or Stepwise Exchange Reactions.

In this class of exchange reaction, only a single hydrogen atom is replaced by a deuterium atom in each molecule which reacts on the surface of the catalyst. Isotopic species containing two or more deuterium atoms are formed only by successive reactions.

Simple exchange reactions are characterised by :-

- (1) An M value of unity (defined by equation 2.8.).
- (2) The only initial product will be the monodeutero species, $C_n H_{m-1} D$.
- (3) Satisfaction of the interconversion equilibria, (equations 2.1 and 2.2), provided that the isotopic species of the hydrocarbon used as reactant are in equilibrium and provided that all hydrogen atoms in the molecule are equally susceptible to exchange (58,59).

Mechanistically a simple exchange process implies that the adsorbed intermediate, whether it is of the dissociation type, $C_n H_{m-1}$, or the associative type, $C_n H_{m+1}$, must be a comparatively stable entity on the surface of the catalyst. There must be little chance of the species undergoing further reaction on the surface as this would give rise to multiple exchange products.

Multiple Exchange Reactions.

In this type of exchange reaction more than one deuterium atom is introduced into the hydrocarbon molecule on each interaction with the catalyst surface. The existence of multiple exchange is recognised in three ways, exactly analogous to those described above for simple

exchange reactions:-

- (1) The "M value" will be greater than unity and will give the average number of deuterium atoms entering each hydrocarbon molecule in the initial stages of the reaction.
- (2) The initial products will contain species having more than one deuterium atom.
- (3) The isotopic distribution, during the course of the reaction, will be richer in the more highly deuterated species than would be expected from the calculated distributions based on equation 2.2.

Product distribution must be measured at low conversions, to exclude (a) species formed by successive interactions with the catalyst if criterion (2) is used and (b) the effect of approaching equilibrium if criterion (3) is used, since at equilibrium the distribution of isotopic species will be the same irrespective of the nature of the exchange process.

Multiple exchange reaction mechanisms are more complicated than those for simple exchange. However, four alternatives may be postulated:-

- (1) Chemisorption of the hydrocarbon only during the actual exchange.
- (2) The formation of a single type of dissociated species involving the loss of at least two hydrogen atoms from the original molecule.
- (3) The formation of a single type of associated species having at least two hydrogen atoms more than the original molecule.

(4) The interconversion, of two or more types of adsorbed species of different states of hydrogenation, on the surface of the catalyst.

A more complete treatment of the above mechanisms along with further aspects of exchange reactions are given by Kemball^(29,60).

2.9. Isotopic Oxygen Exchange.

The exchange of isotopic oxygen with oxide catalysts provides an insight into the mechanistic aspects of oxidation catalysis and may help to elucidate the "oxygen" addition stage of the propylene oxidation reaction. The above technique will be considered in detail under the appropriate chapter.

Oxidation Reactions.

3.1. Introduction.

In recent years the upsurge in demand for synthetic products has led to the growth of catalytic oxidation of hydrocarbons as an important method of synthesis. The majority of oxygenated carbon compounds as well as olefins and dienes can be made by the partial oxidation of abundant hydrocarbon feedstocks. Equilibria in reactions with oxygen are usually very much in favour of the oxygenated or dehydrogenated products, and the major problem is that of obtaining a selective reaction. Reactions presently carried out on an industrial scale include the oxidations of ethylene to acetaldehyde and ethylene oxide, benzene to maleic anhydride, naphthalene to phthalic anhydride, propylene to acrolein and the ammoxidation of propylene to acrylonitrile, to name but a few.

The majority of the industrial oxidation catalysts are metal oxides in which the metal is capable of existing in more than one valency state. In order to obtain high selectivity moderating elements are very often added to the catalysts. Margolis⁽⁶¹⁾, Sampson and Shooter⁽⁶²⁾ and Stone⁽³⁷⁾ have extensively reviewed heterogeneously catalysed hydrocarbon reactions and produced a qualitative classification of oxide catalysts.

3.2. Catalytic Oxidation of Propylene.

The catalytic oxidation of olefins, over a number of different catalysts, has received considerable attention during the past decade.

Those studies have been principally concerned with the oxidation of propylene to form acrolein and with the oxidative dehydrogenation of n-butenes to form 1,3-butadiene. As previously mentioned this investigation is concerned with the catalytic oxidation of propylene to form acrolein using a range of tin-antimony-oxide catalysts. Many results have now appeared in the literature concerning such reactions, and although, the majority have been obtained by the use of bismuth-molybdenum-oxide catalysts, the great similarity between the two catalyst systems renders those results invaluable.

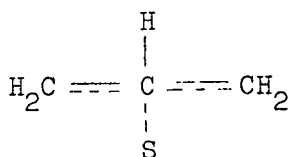
A number of review articles by Margolis⁽⁶¹⁾, Sampson and Shooter⁽⁶²⁾, Voge and Adams⁽⁶³⁾ and Sachtler⁽⁶⁴⁾ have extensively discussed the results.

3.3. Mechanisms of Propylene Oxidation.

Mechanistic studies of the oxidation of propylene have taken several directions, including the consideration of products formed from deuterium labelled propylene, physical studies of the catalyst and tracer experiments using ^{13}C . Initially the problem was tackled by Margolis⁽⁶¹⁾ and co-workers who found interesting relationships between the catalyst work function, oxygen exchange rates and catalytic behaviour as modified by various additives. Further insight into the mechanism of propylene oxidation was given by Voge, Wagner and Stevenson⁽⁶⁵⁾ who oxidised propylene labelled with ^{13}C in the methyl group. The resulting acrolein was found to contain half the heavy carbon in the carbonyl group, even

though the recovered propylene was only slightly isomerised. Their results suggest that, in the reaction sequence, the carbon skeleton, while retaining its chain character, loses the identity of the end carbon atoms. Therefore, the only plausible mechanism is the initial removal of a hydrogen atom from the methyl group to form an allyl intermediate, which subsequently reacts at either end with equal probability.

Similar results and mechanistic conclusions have been obtained by Sachtler⁽⁶⁷⁾, Sachtler and de Boer⁽⁶⁸⁾ and by Godin, McCain and Porter⁽⁵²⁾ using isotopic carbon labelled propylene over bismuth-molybdeum-oxide and tin-antimony-oxide catalysts respectively. These results indicate that the propylene molecule must be dissociatively adsorbed on the catalyst by splitting off a hydrogen atom in the allyl position and forming an allylic complex with a surface ion S.



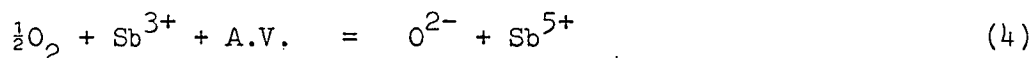
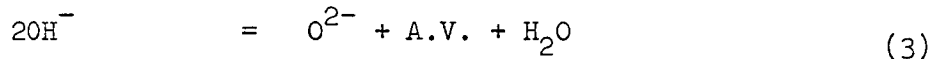
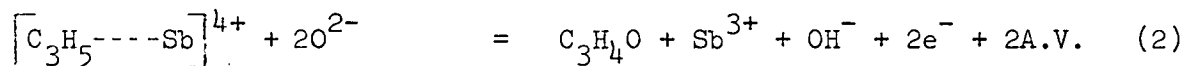
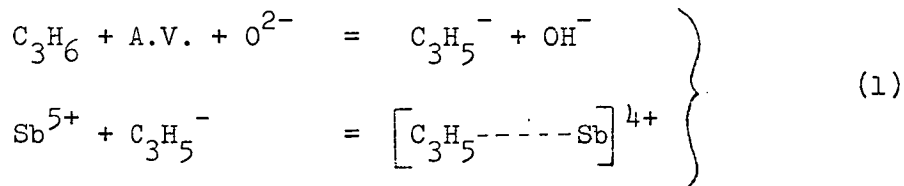
A large amount of experimental evidence has been accumulated to show that many oxidations occur by removal of a hydrogen atom from the allylic position. This is to be expected, provided reaction does take place by H atom removal, as both experiment and theory show that the allylic C-H bond is weaker than most other C-H bonds in hydrocarbons by 60-80 kJ mole⁻¹ (66).

Confirmation and extension of this mechanism was obtained by Adams and Jennings^(50,69) using propylene labelled with deuterium in various positions. Their proposed mechanism, based on kinetic isotope data, suggested that the initial abstraction of an allylic hydrogen to form a symmetric allyl intermediate was followed by a second hydrogen abstraction from either end of this intermediate, followed by hetero atom incorporation. Their observed kinetic isotope effects showed clearly that the first hydrogen abstraction was the slow rate determining step. Adams⁽⁶⁶⁾ has further suggested that chemisorbed oxygen atoms are the abstracting agents. It has also been proposed by the same authors that the initial oxidative abstraction has no carbonium ion characteristic and that the same step wise mechanism is involved in the formation of acrolein and acrylonitrile. Acrolein does not, however, appear to be an intermediate in the ammoxidation of propylene to acrylonitrile. Further confirmation of these results has recently been obtained by Grasselli and Suresh⁽⁸⁵⁾ as a consequence of work carried out on uranium-antimony-oxide catalysts.

Conflicting evidence has recently been produced by Cant and Hall^(70,71), as a result of studies carried out over metal catalysts. They suggest that another mechanism, in which oxygen is added before the abstraction of the second hydrogen atom, may also be operative. A similar mechanism was proposed earlier by Margolis⁽⁶¹⁾. Thus, depending on the catalyst, several mechanistic schemes may be in simultaneous operation.

In addition it is becoming increasingly evident that homogeneous gas phase reactions may further complicate the reaction. McCain and Godin⁽⁷²⁾ observed that propylene oxide was formed via a homogeneous pathway in the postcatalytic volume during the catalytic oxidation of propylene over a bismuth-molybdenum-oxide catalyst. Keulks⁽⁷³⁾ et al have recently reported that during the partial oxidation of propylene to acrolein, over bismuth molybdate, acrolein subsequently underwent a number of homogeneous reactions in the postcatalytic volume. Friedli⁽⁷⁴⁾ et al studied the oxidative dehydrodimerisation of propylene and isobutene over manganese oxide, (a reaction similar to the oxidative dehydrogenation of olefins, and believed to have the abstraction of an allylic hydrogen to form an allylic intermediate as the rate determining step), and were able to detect allyl radicals in the gas phase. Margolis⁽⁷⁵⁾ has recently suggested a pathway for propylene oxidation, over tin-molybdenum-oxide catalysts, based on desorbed allyl radicals. Keulks⁽⁷⁶⁾ et al have presented evidence for a surface initiated homogeneous reaction, over bismuth-molybdenum-oxide catalysts, which results in an enhanced conversion of propylene to acrolein and to the formation of propylene oxide. Allyl peroxide or allyl hydroperoxide species, formed on the surface, are suggested as possible initiators for the homogeneous reaction. Their proposed reaction mechanism scheme is shown below:-

is as follows. This mechanism attempts to link catalyst structure and participation with the overall oxidation reaction.



$\left[\text{C}_3\text{H}_5\text{-----Sb} \right]^{4+}$ represents an allyl anion

π bonded to Sb^{5+} and A.V. is an anion vacancy. The site of propylene oxidation is believed to be an Sb^{5+} ion surrounded by oxygen ions in octahedral co-ordination. Reaction (2) is probably a two step process with hydrogen abstraction from the allyl anion before introduction of the oxygen atom. A somewhat similar mechanism has been proposed by Batist⁽⁷⁹⁾ et al for bismuth-molybdenum-oxide catalysts.

3.4. The Acrylonitrile Process.

British Petroleum Chemicals International Limited operate a continuous process for the manufacture of high purity acrylonitrile monomer. The process depends on the reaction of propylene, ammonia

and air, at 640-755 K, over a mixed oxide catalyst related to those studied in this thesis.

The products consist of acrylonitrile along with minor amounts of acetonitrile and hydrogen cyanide, the crude acrylonitrile being purified by distillation to yield 98+% liquid. The process, whose flow diagram is shown in Figure 3.1⁽⁸⁰⁾, operates on a once-through basis without the need for recirculation.

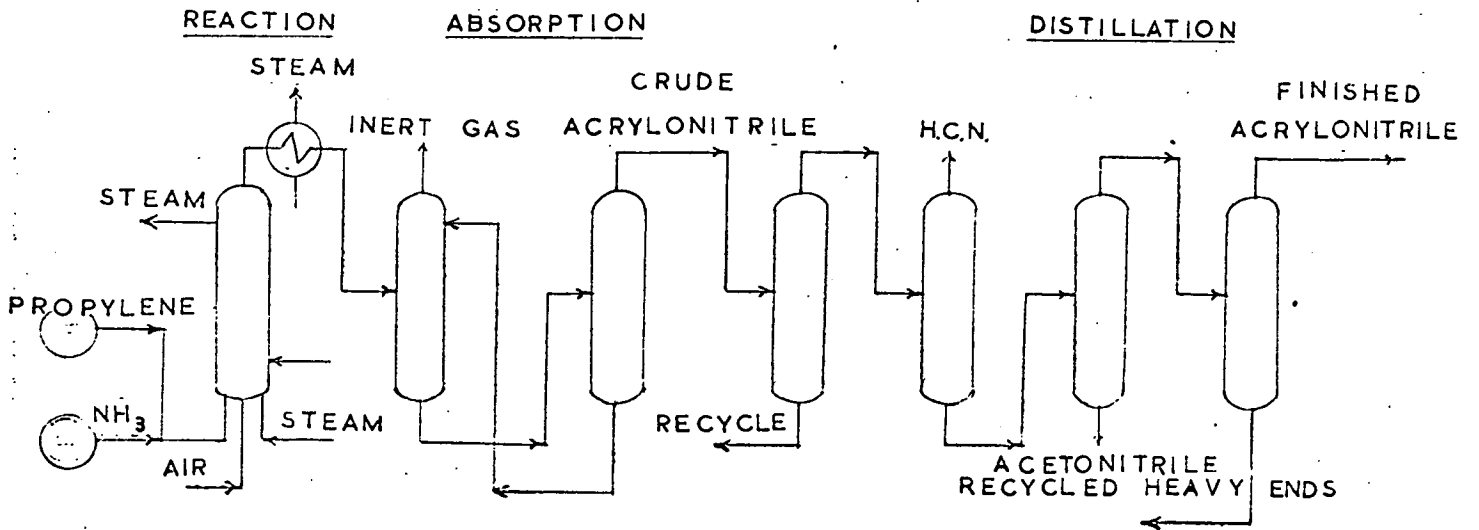


FIGURE 3.1

PART II

EXPERIMENTAL AND RESULTS

CHAPTER 4

Experimental Apparatus and Techniques.

4.1. Introduction.

The apparatus used in this investigation was designed to study exchange reactions of hydrocarbons and heavy water over metal oxide catalysts in a static system. A basically similar piece of apparatus, with a few minor modifications was used to study $^{16}\text{O}_2 / ^{18}\text{O}_2$ exchange reactions and propylene / $^{18}\text{O}_2$ oxidation reactions over the same catalysts. The apparatus consisted essentially of three parts:-

- (1) A high vacuum gas handling system which enabled mixtures of pure gases and liquid vapours of definite composition and pressure to be prepared.
- (2) A combined reaction vessel and capillary leak.
- (3) A mass spectrometer linked directly to the reaction vessel, via the capillary leak, which enabled continuous analysis of the gas mixture in the reaction vessel.

4.2. Gas Handling System.

A diagrammatic representation of the gas handling system is shown in Figure 4.1. It consisted of a general purpose high vacuum system, constructed throughout from "Pyrex" glass, with ground glass taps and joints, lubricated with "Apiezon L" high vacuum grease. The complete system could be evacuated to a pressure of 1.33×10^{-7} kNm⁻² (10^{-6} mm Hg) by means of an electrically heated ~~single~~ ^{two-} stage mercury diffusion pump,

OXYGEN - 18 HANDLING SYSTEM

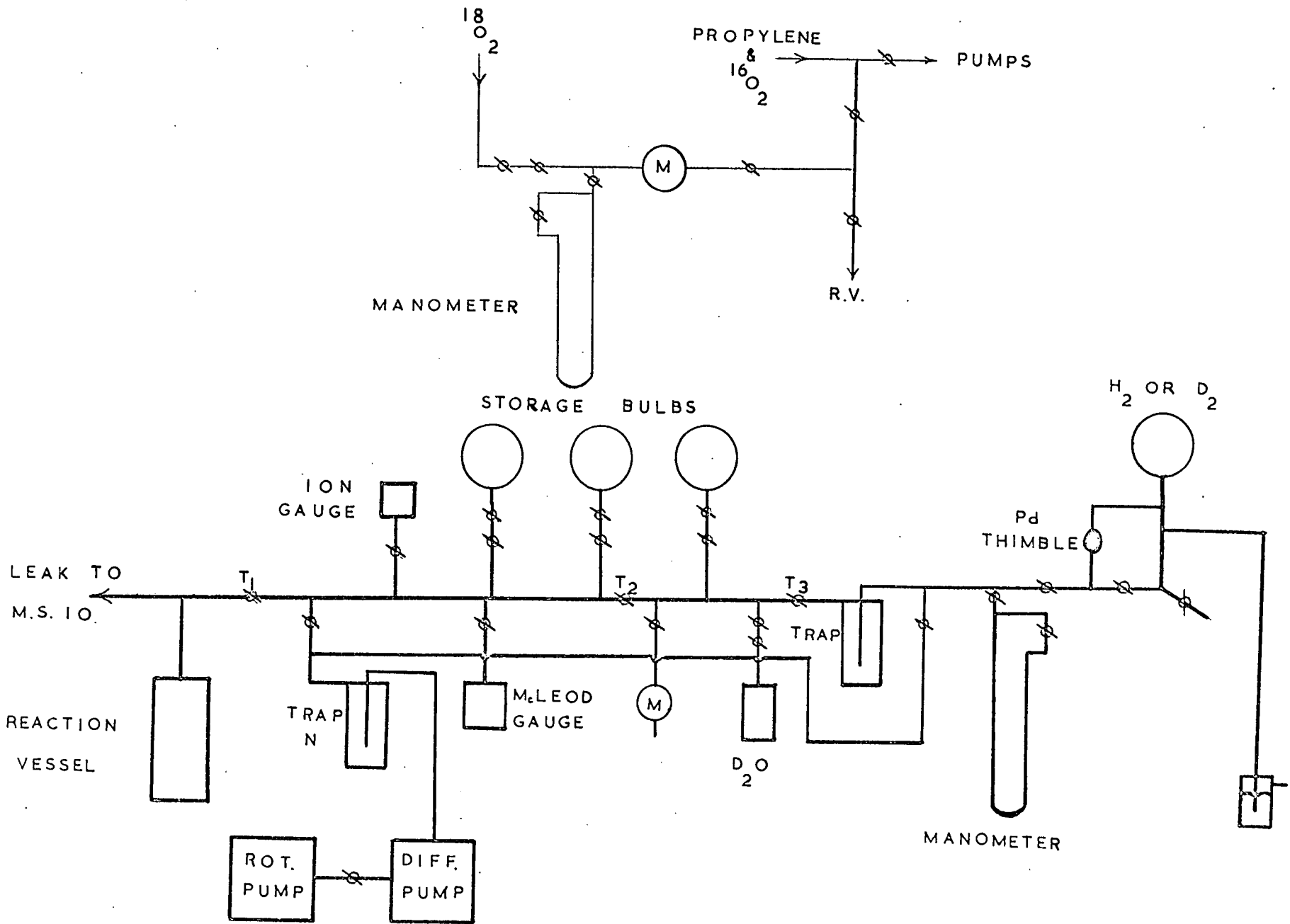


FIGURE 4.1 GAS HANDLING SYSTEM

backed by a two-stage "Speedivac" rotary pump. Mercury was excluded from the gas line by means of the liquid nitrogen trap 'N' and the pressure was measured by a McLeod gauge.

The reactants, whether liquids or condensable gases, were purified by trap to trap vacuum distillation then stored in the appropriate storage bulbs or tubes. Hydrogen or deuterium gas was purified by diffusion through a heated palladium thimble. Gaseous mixtures of condensable gases and heavy water were prepared by admitting the required pressure (P_1) of one component into the mixing volume (M) then filling a portion of the gas line (G) with a calculated pressure of gas (P_2) required to give the requisite pressure when frozen into the mixing volume. The accuracy of the prepared gaseous mixture could be checked by measuring the total pressure in the mixing volume. Pressures were measured by means of a mercury manometer. Mixtures of non-condensable gases were prepared by admitting the required pressure (P_1) of one component into the mixing volume (M) then filling a portion of the gas line (G) with a calculated pressure of gas (P_3) ($P_3 > P_1$) such that expansion of (P_3) into the mixing volume (M) would equalise the pressures, without significant diffusion of the first component out of (M), and give the desired ratio of reactants in the mixing volume. The prepared mixtures were allowed to stand overnight, to improve their homogeneity, before being expanded into the reaction vessel.

4.3. Reaction Vessel and Capillary Leak.

The reaction vessel was constructed from "Pyrex" glass, or silica glass for high temperature work, and was joined to the apparatus

by means of a B24 ground glass joint which fitted into a water cooled socket. Temperature control of the reaction vessel to within ± 0.5 K was achieved by the use of a close fitting furnace combined with a "Variac" voltage controller and a Fielden Electronics "Bikini" temperature controller. Temperatures were measured by a chromel-alumel thermocouple attached to the reaction vessel. The oxidation apparatus employed a "Eurotherm" temperature controller unit, the thermocouple of which fitted into a pocket within the reaction vessel, just above the catalyst surface.

Continuous analysis of the gas mixture was effected by means of a fine tapering capillary leak, similar in design to one used by Nier⁽⁸¹⁾, attached to the top of the reaction vessel opposite the inlet tube. This leak led directly into the analyser tube unit of the mass spectrometer, thus, enabling a small continuous gas stream to be drawn into the mass spectrometer. The capillary leak was constructed from "Pyrex" glass by partially collapsing a section of 8 mm bore tube and drawing it out to a fine capillary whose length was then adjusted to give a leak rate of 2.67 k Nm^{-2} (20 mm Hg) air into a volume of 20 ml in 20 minutes with a pressure difference of 101.32 k Nm^{-2} (one atm). A capillary leak which fulfilled the preceding requirements was found to provide an adequate sample for mass spectral analysis over a period of 12 hours without any appreciable depletion of gas in the reaction vessel. The capillary leak employed for the oxidation experiments had a leak rate five times faster than the one previously described; the pumping rate for the mass spectrometer was also increased by a factor of five. A

further modification for the oxidation apparatus was that the capillary leak extended downwards into the reaction vessel and terminated just above the catalyst surface.

The design and properties of capillary leaks have been discussed by various authors⁽⁸²⁻⁸⁴⁾ and the conclusions reached were that gas flow through a capillary leak can occur by two processes:-

(1) Viscous flow.

(2) Molecular flow.

If viscous flow predominates, the gas leaking into the mass spectrometer will have the same composition as that in the reaction vessel, however, if molecular flow is occurring there will be discrimination against the higher mass elements in the gas mixture. Thus, a satisfactory leak should permit only viscous flow.

In the study of exchange reactions it is assumed that the relative amounts of the various isotopic hydrocarbons leaking into the mass spectrometer exactly mirror the composition of the gas in the reaction vessel. The error in this assumption is usually small as the masses of the isotopic species are similar and molecular flow offers only a slight contribution. The only exception being where the gases analysed differ markedly in size, as with hydrogen and deuterium. It is unlikely that diffusion to and from the catalyst surface is rate determining, or that any appreciable time lag existed between the molecules leaving the surface, and their appearance in the mass spectrometer.

4.4. The Mass Spectrometer.

An A.E.I. model M.S.10 mass spectrometer was used for analysis of the reaction mixtures and is represented diagrammatically in

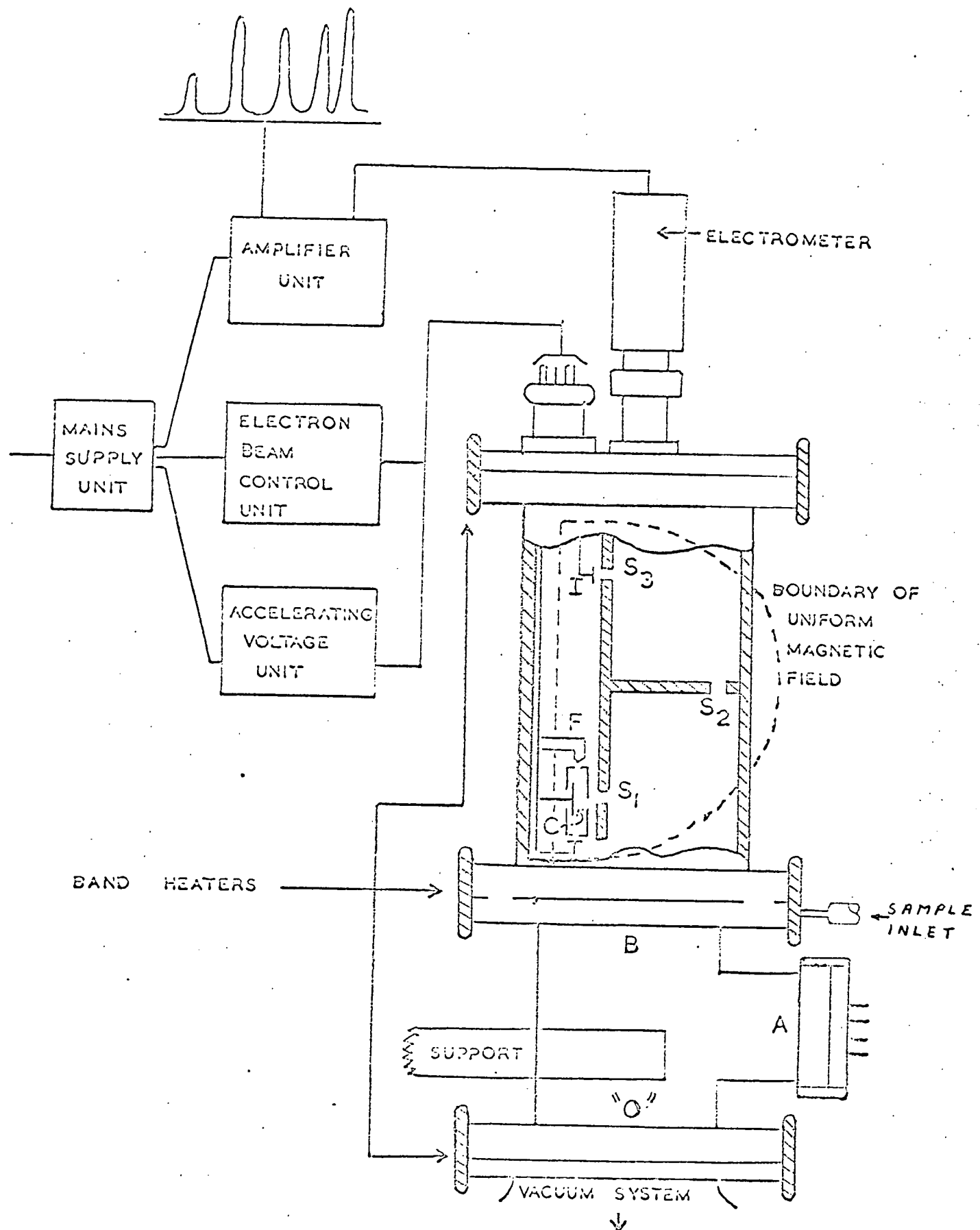


FIG. 4.2 MS10 MASS SPECTROMETER

Figure 4.2. The gas was leaked, via the capillary leak, into the analyser tube unit and thence into the ion source "C" where it was ionised by electrons produced by the electrically heated rhenium filament "F". The ions were then accelerated through the slit "S₁", into the uniform magnetic field, by an accelerating potential. Equation 4.1 indicates that with a constant accelerating voltage and a constant magnetic field the ions follow semicircular paths the radii, R, of which vary with the m/e ratio of the ions.

$$\frac{m}{e} = R^2 H^2 / 2V \quad 4.1$$

where H is the magnetic field strength and V is the accelerating voltage. By variation of either the magnetic field or the accelerating voltage all the ions of one m/e ratio could be focussed through the defining slit "S₂" and the collector slit "S₃" onto the collector plate "I".

The ion current was preamplified by means of an electrometer head type ME 1403 with an input resistance of 10^{11} ohms and a time constant of 1 second. The signal was then further amplified and displayed as a trace on a "Servoscribe" pen recorder. A sensitivity range changing control enabled each peak to be measured and recorded at its maximum sensitivity. The uniform magnetic field was supplied by a permanent magnet of approximately 1840 gauss.

The ion chamber of the mass spectrometer could be evacuated to a pressure of 1.33×10^{-9} kNm⁻² (10^{-8} mm Hg) by means of a "Metrovac" 033 water cooled oil diffusion pump backed by a "Metrovac" GDR1 two stage rotary pump. A variable orifice plate located at "O" reduced the pumping speed to 1 litre sec⁻¹. A liquid nitrogen trap prevented

oil from the diffusion pump reaching the ion chamber. The pressure inside the ion chamber was measured by an A.E.I. VC20 ionisation gauge. For the oxidation experiments an A.E.I. model M.S.20 mass spectrometer was employed, this instrument being merely an updated version of the previously described M.S.10.

4.5. Volume Calibrations.

A bulb of known volume, determined by calibration with water, was attached to the gas line by means of a ground glass joint. The bulb was then filled with air, to a pressure measured on the manometer, and the tap to the bulb closed. The remainder of the apparatus was evacuated, then, by successive expansions into the various parts of the apparatus the corresponding volumes were obtained by the application of Boyle's Law at the desired temperatures.

A similar method, used to double check the calculated volumes, employed a calibrated McLeod gauge to read off the successive expansions of gas into the appropriate parts of the apparatus. A further refinement was the use of helium gas as it is not appreciably adsorbed on to the glass.

Important apparent volumes are given below: -

Volume of the reaction vessel	at 296 K	195.0 ml.
Volume of the mixing bulb	at 296 K	313.5 ml.
Volume between tap 1 and tap 2	at 296 K	36.2 ml.
Volume between tap 1 and tap 3	at 296 K	60.0 ml.
Volume between tap 1 and manometer	at 296 K	175.0 ml.

Knowing the partial pressures of the reactants and the appropriate volumes, the pressure of gas and hence the number of molecules in the reaction vessel could be calculated at any temperature.

4.6. Materials.

The materials used in the catalyst preparations were Fry's pure powdered tin and pure powdered antimony from Associated Lead. All the reagents used in the preparations were of "Analar" grade.

Reactants.

The propylene and isobutene were Matheson Company C.P. Grade reactants while the D_2O was obtained from B.D.H. (99.7% pure). All the other reactants, such as acrolein (B.D.H.) and CO_2 used for relative sensitivity measurements, were obtained in as pure a state as possible. Each compound was subjected to a number of freeze-thaw and outgassing cycles prior to trap to trap vacuum distillation before use, the middle third only being retained. Oxygen -16 was used as supplied by B.O.C. while the oxygen -18 (O-17 = 0.58 atom %, O-18 = 91.00 atom %) was supplied by Yeda R & D Co. Ltd., Rehovoth, Israel. The deuterated propylenes were kindly supplied by British Petroleum Chemicals International Limited, Epsom Division.

4.7. Catalyst Preparation.

A representative number of tin-antimony-oxide catalysts were prepared by taking different proportions from two large batches of precipitated tin oxide and antimony oxide. Each composition was

then thoroughly mixed, washed, dried, pelleted and heat treated.

Preparation of Stannic Oxide.

1,450 g of Fry's pure powdered tin was added over a period of 50 minutes to a mixture of 5.46 l HNO_3 and 18.32 l water at 373 K, while stirring. The mixture was maintained at 373 K for a further 30 minutes then cooled. The white gelatinous precipitate of tin oxide was filtered off and thoroughly washed with distilled water, prior to storage under water.

Preparation of Antimony Oxide.

692.2 g of pure powdered antimony (Associated Lead) was added over a period of 50 minutes to 2.85 l HNO_3 at 373 K, while stirring. The mixture was maintained at 373 K for a further 30 minutes and was then cooled. The pale yellow precipitate of antimony oxide was filtered off and thoroughly washed with distilled water, prior to storage under water.

Preparation of the Tin-antimony-oxide mixtures.

Various proportions of the above two wet precipitates were taken to give the required mixtures. The combined precipitates were thoroughly mixed in the form of a slurry, filtered off, washed with 3 l distilled water, dried overnight at 383 K and finally ground to pass a 100 mesh sieve.

Pelleting.

Each composition was mixed with 1% w./w. graphite (Avarc Pure Flake No. 3) as lubricant and pelleted to 1/16" x 1/8" pellets.

Heat Treatment.

The pellets were then heat treated in air at 1123 K in stainless steel baskets. The heat treatment programme consisted of a temperature rise from room temperature to 1123 K at a rate of 20 K hr⁻¹ followed by a heat soak at 1123 K for 16 hours. After that time the pellets were slowly cooled to room temperature.

Analysis.

X-ray fluorescence analysis, for tin and antimony, was carried out on samples of the heat treated pellets. Debye-Scherrer X-ray powder photographs showed that the heat treated compositions were heterogeneous, consisting of SnO₂, α-Sb₂O₄ and minor amounts of β-Sb₂O₄.

Surface Area.

Surface areas were measured by the standard B.E.T. method using nitrogen as adsorbate on (1) the powders after drying at 383 K and (2) on the pellets after heat treatment at 1123 K. Pore volume distribution measurements were also carried out on the heat treated pellets*.

The analysis and surface area results are shown in Table 4.1.

* Footnote:- The author is indebted to Miss B.J. Graves of British Petroleum Chemicals, Epsom Division, for her assistance with this part of the experimental work.

Table 4.1

Nominal Atom % Sb *	X-ray fluorescence Analysis of H.T. Pellets, Atom % Sb	Surface Area m ² /g	
		Powder Dried at 383 K	Pellets H.T. at 1123 K
0	0	132.2	4.2
3	3.30	-	9.9
5	6.13	141.9	12.2
7.5	7.40	-	18.1
10	9.09	136.2	19.2
20	19.60	-	20.8
26	26.80	-	18.4
30	29.60	121.0	15.4
50	49.50	92.7	12.5
75	75.00	45.5	7.0
100	100	3.8	0.9

* Atom % Sb = Atomic Ratio $\frac{\text{Sb}}{\text{Sb} + \text{Sn}} \times 100$

4.8. Infrared Spectroscopy.

All the infrared spectra shown in this thesis were run on a Perkin-Elmer 225 spectrometer. A standard 10 cm. path length infrared gas cell fitted with potassium bromide windows and a cold finger, for condensation of the gaseous reactants, was used throughout. The appropriate experimental conditions and techniques will be discussed in a later chapter.

CHAPTER 5

Exchange Reactions of Unsaturated Hydrocarbons with Heavy Water.

5.1. Introduction.

The catalytic oxidation of olefins, principally propylene and the butenes, over a number of metal oxide catalysts, has received considerable attention during the past decade. The mechanism by which propylene reacts, at least initially, over cuprous oxide, bismuth-molybdenum-oxide mixtures, uranium-antimony-oxide mixtures and tin-antimony-oxide mixtures has been extensively discussed in recent papers^(52,61,62,63,64 and 85). However, there still remains a degree of uncertainty as to the exact nature of propylene oxidation over mixed tin-antimony-oxide catalysts, even though these catalysts form the basis of a commercial acrylonitrile process.

A study of the behaviour of the carbon-hydrogen bond in propylene, by means of the catalytic exchange reaction between propylene and heavy water, should help to clarify the nature of the active intermediate with regard to the initial steps in the overall oxidation reaction. The choice of heavy water as the deuterated reactant not only emphasised the relevance of the experiment to the full scale oxidation process, but also prevented serious reduction of the catalyst under investigation, as would have occurred with deuterium. It should also be noted that the activation of heavy water for exchange reactions is easily accomplished⁽⁸⁶⁾.

5.2. Experimental.

The experimental apparatus and catalyst preparation has been described previously, (Chapter 4). Reactions were carried out in a "Pyrex" glass reaction vessel at temperatures between 294 and 673 K. The reaction mixture, three parts heavy water to one part propylene was prepared in the mixing bulb and allowed to stand overnight, prior to expansion into the reaction vessel. The initial pressure in the reaction vessel was 1.20 k Nm^{-2} (9 mm Hg). Normally, fresh 1 g samples of catalyst, (in powder or pellet form), were used in each experiment. The catalyst was activated by outgassing in vacuo for 18 hours at 673 K, then cooled to the reaction temperature prior to admission of the reaction mixture. In some cases, successive runs were carried out on the same catalyst sample, with brief outgassing between the runs, while in others, fresh samples, after outgassing, were pretreated at the reaction temperature with 0.53 k Nm^{-2} (4 mm Hg) propylene for 60 minutes, followed by 10 minutes pumping prior to admission of the reaction mixture.

The exchange reaction was followed by monitoring the peaks with m/e values from 36 to 48, while acrolein was detected from peaks 55 to 57. To minimise fragmentation of propylene in the mass spectrometer an ionizing voltage of 15 eV was used. After the required corrections had been made to the mass spectral data for background, natural isotopes and fragmentation, (see Chapter 2.2), the percentage of each isotopic species was obtained as a function of time.

5.3. Results.

5.3.1. Propylene/D₂O Exchange.

Control experiments proved the "Pyrex" glass reaction vessel to be catalytically inert for the propylene/D₂O exchange reaction at temperatures up to 673 K. Preliminary experiments indicated that the rate of exchange at temperatures around 473 K would be satisfactory for continuous mass spectrometric analysis.

At 473 K the propylene/D₂O mixture was found to react over all but the 100 atom % Sb catalyst, the rate of ^{constant} reaction, (as defined in equations 2.5 and 2.6), decreasing with time, as shown by the typical, curved, first order rate plot in Figure 5.1. It may be noted that curvature was not pronounced until approximately 60% of reaction was completed. The decrease in the activity of the catalyst was accompanied by a marked reduction in the total amount of isotopic propylenes in the gas phase. The loss in some extreme cases amounted to 50% after 5 hours. Initially a small quantity of acrolein was produced, but no further increase was observed during the course of the reaction. Successive runs on the same catalyst served only to further reduce the activity of the catalyst.

Pretreatment of a fresh, outgassed, catalyst sample, by exposure to propylene at the reaction temperature, prior to admission of the reaction mixture, resulted in a steady rate of exchange, with linear first order rate plots for both $\log (d_o - d_{o_\infty})$ and $\log (\phi_\infty - \phi)$ Vs. time, being obtained as shown in Figures 5.2 and 5.3. During the propylene pretreatment process it was noted that about 10% of the propylene disappeared from the gas phase, presumably on to the catalyst

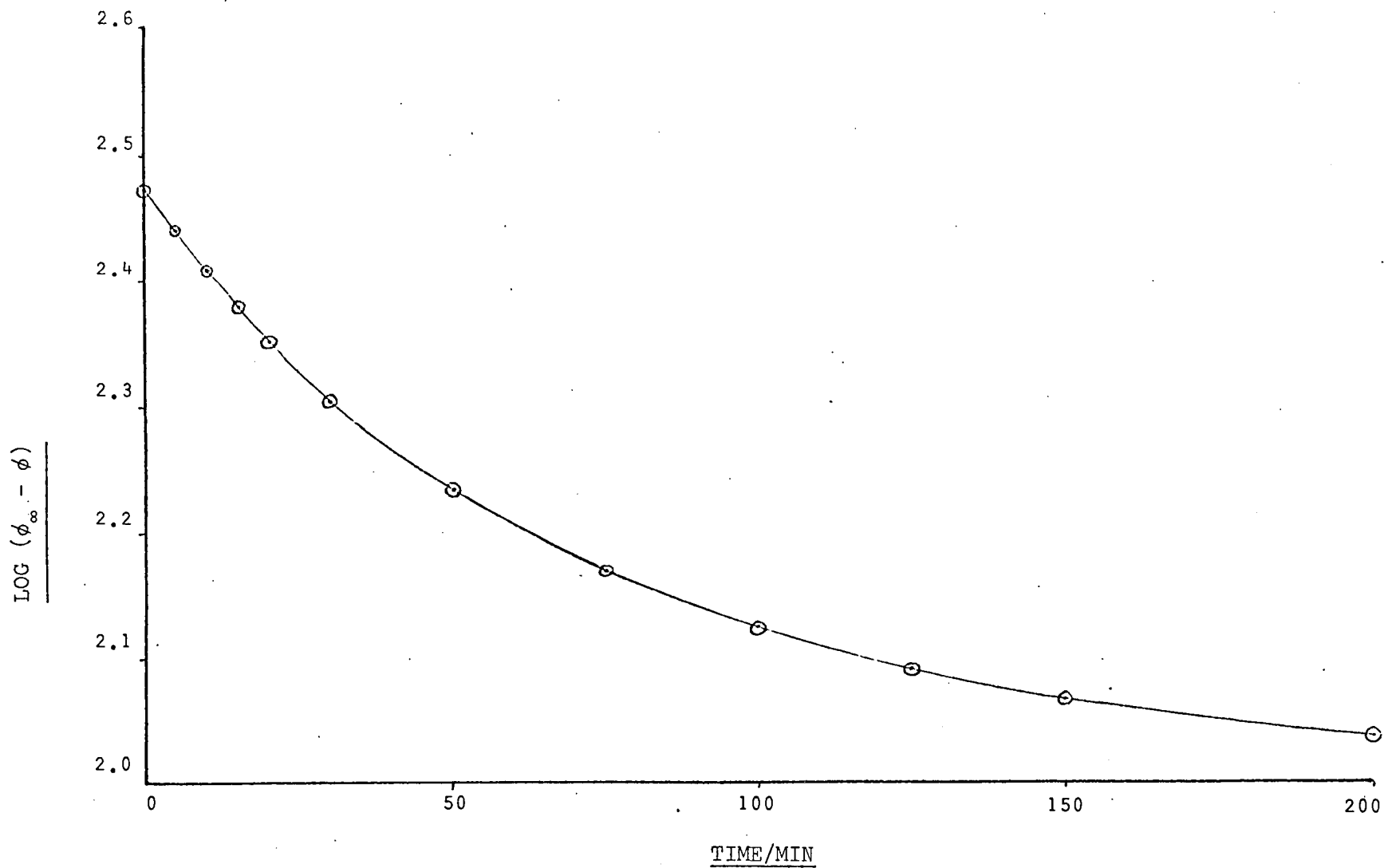


Figure 5.1 First Order Rate Plot ($k\phi$) For Propylene/ D_2O Exchange on Non-treated 9.09 Atom % Sb Catalyst at 473 K.

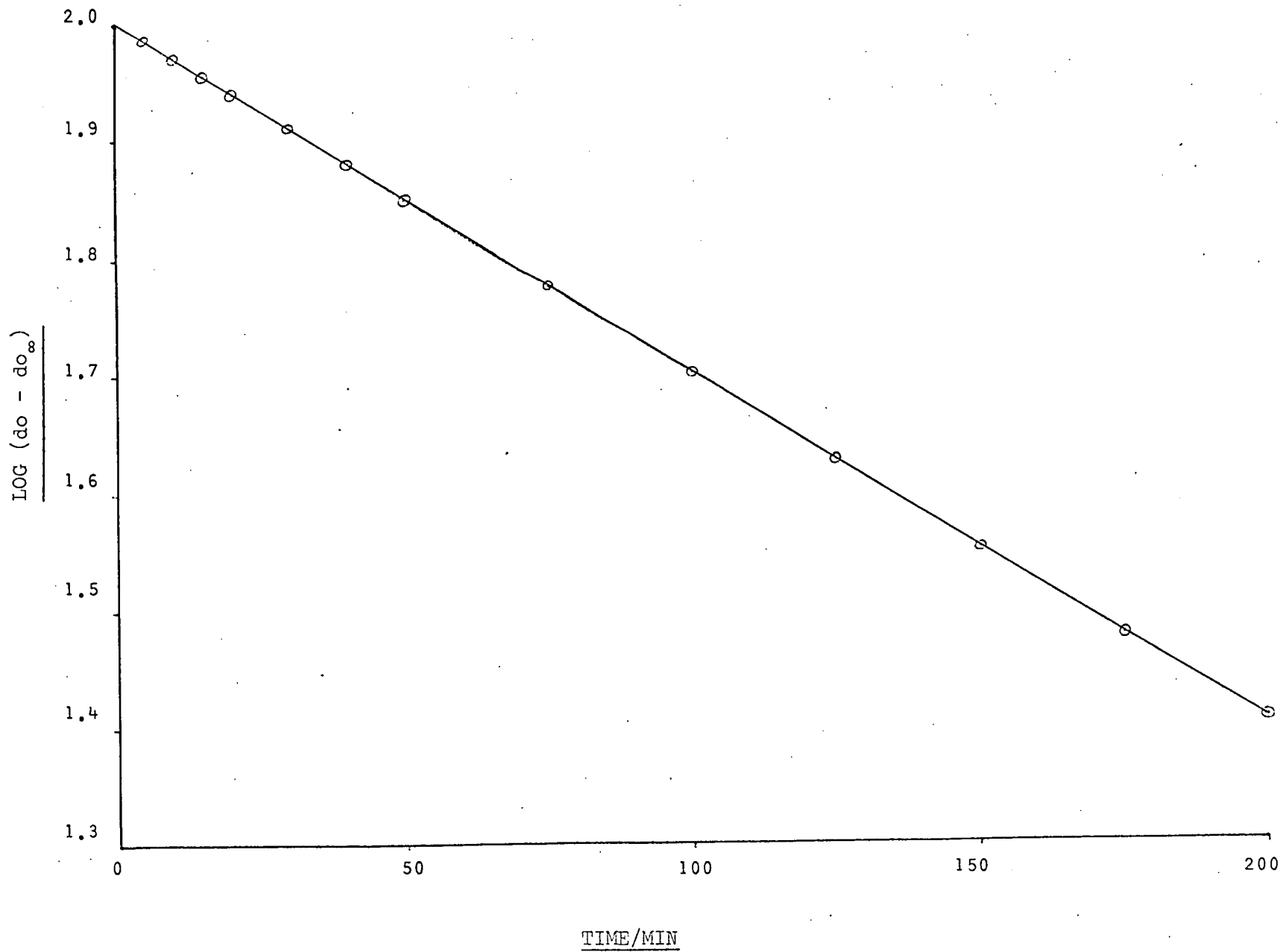


Figure 5.2 First Order Rate Plot (ko) For Propylene/D₂O Exchange on Propylene Pretreated 9.09 Atom % Sb Catalyst at 473 K.

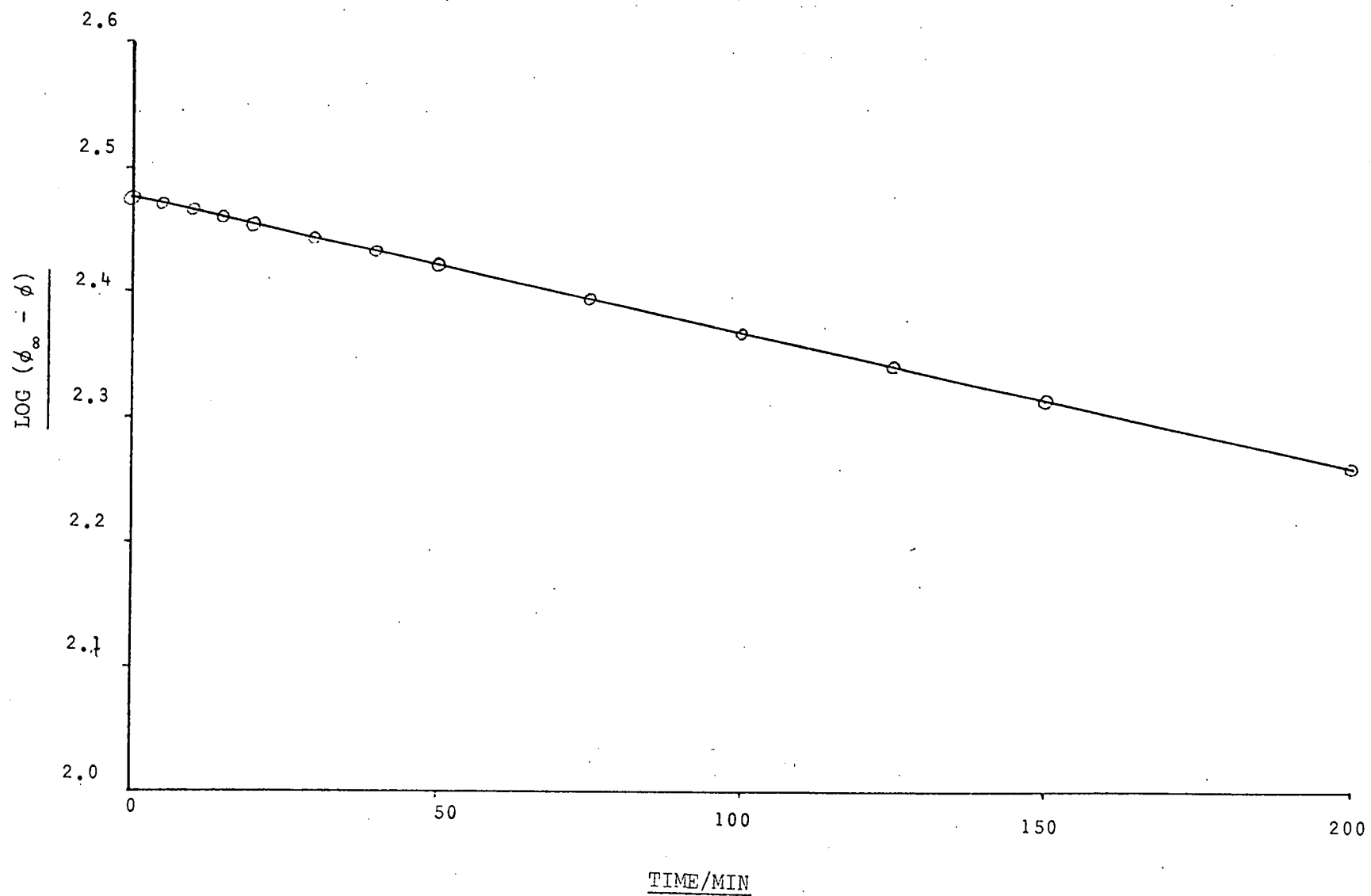


Figure 5.3. First Order Rate Plot ($k\phi$) For Propylene/ D_2O Exchange on Propylene Pretreated 9.09 Atom % Sb Catalyst at 473 K.

surface. For the 9.09 atom % Sb catalyst, the rate constant $k\phi$ was less, by a factor of 7, than the $k\phi$ rate constant obtained from the initial slope of the $\log(\phi_{\infty} - \phi)$ plot for a run on the non-treated catalyst, at the same temperature.

During the course of runs using pretreated catalysts, no acrolein was detected and loss of propylene from the gas phase was considerably reduced, being typically around 10-20% after 5 hours. In all cases, whether the catalyst was pretreated or not, regeneration of the catalyst, to its original activity, could be effected by heating in air for two hours at 673 K. Experimentally it was found that reproducible results could be obtained over all the catalysts, regardless of the particular pretreatment procedure.

In all the exchange reactions of propylene and heavy water on the catalysts, stepwise replacement of hydrogen by deuterium was evident, the only initial product being the monodeuterated species. A typical display of the percentage distribution of isomers plotted against time for the propylene/D₂O exchange reaction is shown in Figure 5.4 for a 9.09 atom % Sb catalyst at 473 K. In every case only five of the six propylene hydrogen atoms were exchangeable. Under no circumstances did the sixth hydrogen atom undergo exchange. Figure 5.4 clearly shows the formation of the five deuterated species.

Further confirmation of the stepwise mechanism was obtained from an inspection of the isotopic distributions at various stages of the reaction. Table 5.1 shows a typical experimental distribution compared with a calculated binomial distribution based on five

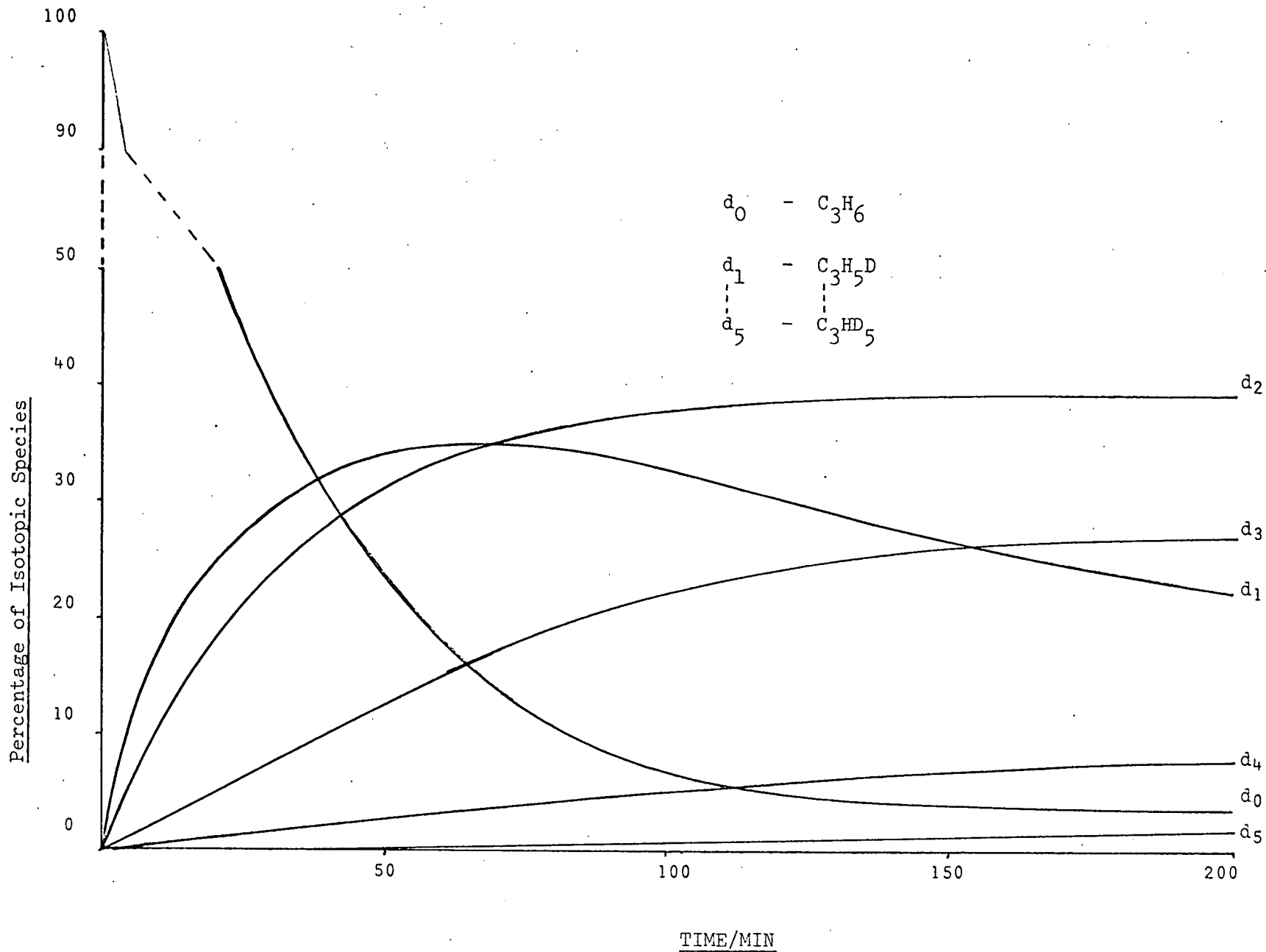


Figure 5.4 Distribution of Isomers For Propylene/ D_2O Exchange on Non-treated 9.09 Atom % Sb Catalyst at 473 K.

exchangeable hydrogen atoms.

TABLE 5.1

Calculated and Experimental Distributions of Propylenes.

	percentage of isotopic species						ϕ
	d_0	d_1	d_2	d_3	d_4	d_5	
Experimental *	6.3	23.3	34.5	25.3	9.0	1.6	211.0
Calculated	6.4	23.5	34.4	25.2	9.2	1.4	211.0

* After reaction on 9.09 atom % Sb catalyst for 200mins. at 473 K.

The value of ϕ indicates the extent of the exchange reaction.

Final confirmation of a simple or stepwise mechanism was obtained by comparing the two first order rate constants $k\phi$ and k_0 where

$$M = \frac{k\phi}{k_0} \quad (\text{equation 2.8})$$

An M value of one, (see table 5.2), confirmed the stepwise mechanism. Evidence to show that the five exchangeable hydrogen atoms in propylene all react at the same rate, was obtained by comparing the experimental distributions obtained after discrete extents of reaction, with the theoretically calculated distributions for the stepwise exchange of a molecule containing five equally reactive hydrogen atoms. Good agreement between the theoretical and experimental distributions was

found over the whole extent of reaction. These results were in good agreement with the work of Buiten⁽⁷⁷⁾ on tin-molybdenum-oxide catalysts.

Runs on fresh 1 g samples of the 9.09 atom % Sb catalyst pretreated with propylene were carried out at a number of temperatures in order to obtain the relevant Arrhenius parameters. Table 5.2 summarises the reaction rate constants and M values at different temperatures.

TABLE 5.2

Temperature K	k_0 % min ⁻¹	$k\phi$ *	M
438	0.35	0.36	1.01
453	0.45	0.46	1.04
473	0.69	0.72	1.04
493	0.91	0.91	1.00

* The $k\phi$ value is equivalent to the number of deuterium atoms entering 100 molecules of hydrocarbon in unit time.

An Arrhenius plot was constructed by plotting $\log k_0$ against $\frac{K}{T}$ as shown in Figure 5.5, and from this the activation energy was found to be 33.2 k J mole⁻¹. A similar result was obtained by plotting $\log k\phi$ against $\frac{K}{T}$. The Arrhenius parameters obtained from the plot

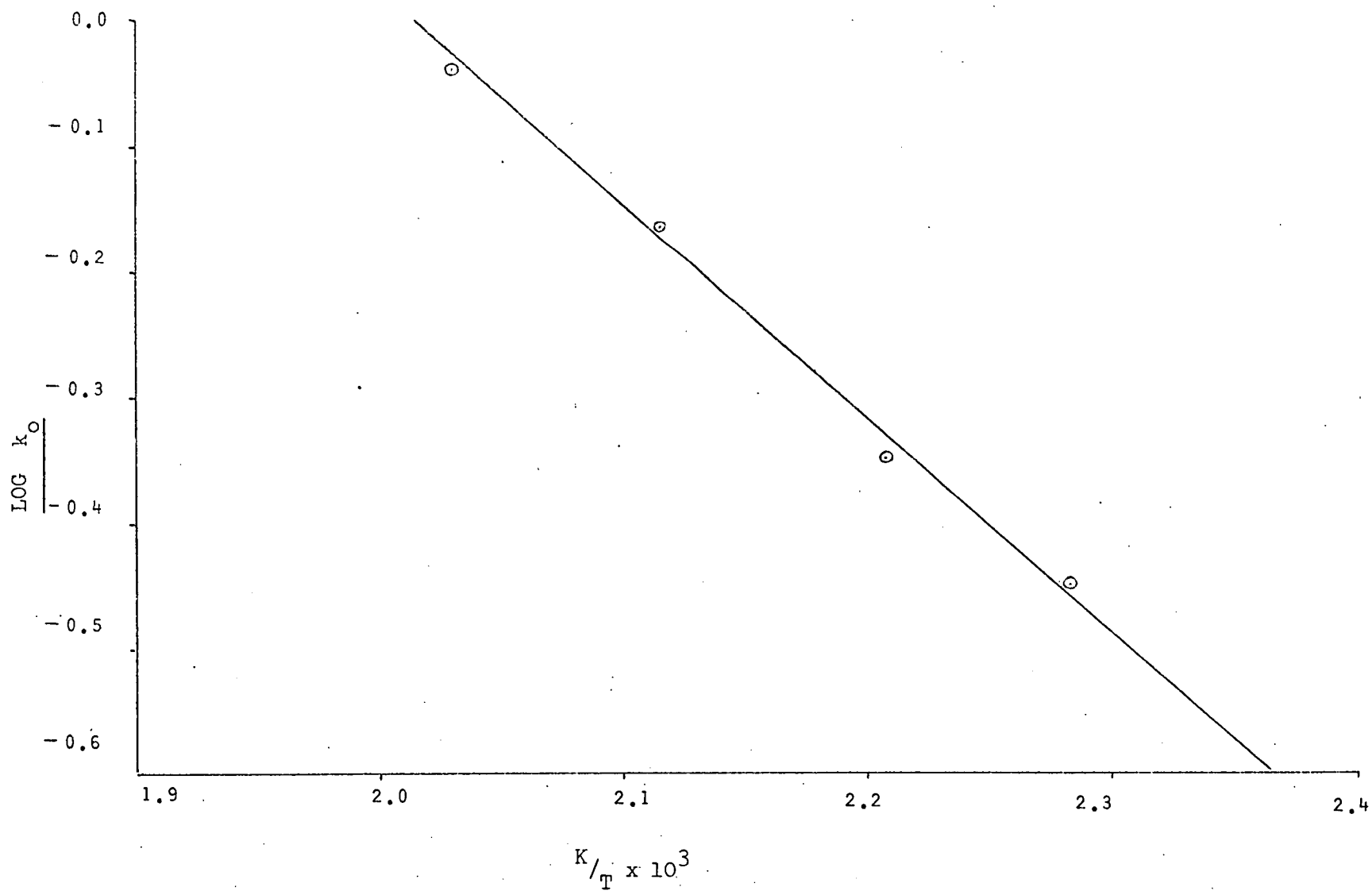


Figure 5.5 Arrhenius Plot For Propylene/D₂O Exchange on Propylene Pretreated 9.09 Atom % Sb Catalyst.

correspond to the equation

$$r_o = 10^{17.39} e^{-33.2/RT}$$

where r_o is the absolute rate in molecules $\text{sec}^{-1} \text{m}^{-2}$ and the activation energy is given in kJ mole^{-1} .

Pretreatment of a fresh, outgassed, catalyst with heavy water, (0.93 k Nm^{-2} (7 mm Hg), 60 min.), at the reaction temperature, prior to admission of the reaction mixture, resulted in an increase in the initial rate constants $k\phi$ and k_o . For the 9.09 atom % Sb catalyst the initial rate constant k_o , at 473 K, was greater by a factor of 20, than the corresponding k_o value for the propylene pretreated catalyst under similar conditions. However, the first order rate plots did tend to curve off after approximately 90% of the reaction had been completed, as shown in Figure 5.6.

TABLE 5.3

Comparison of initial first order rate constants for the 9.09 atom % Sb catalyst at 473 K.

Temperature K	Catalyst Treatment	$k\phi$ *	k_o % min^{-1}	M
473	non treated	4.93	4.02	1.23
473	propylene pretreated	0.72	0.69	1.04
473	D_2O pretreated	14.2	14.0	1.01

* $k\phi$ value is equivalent to the number of deuterium atoms entering 100 molecules of hydrocarbon in unit time.

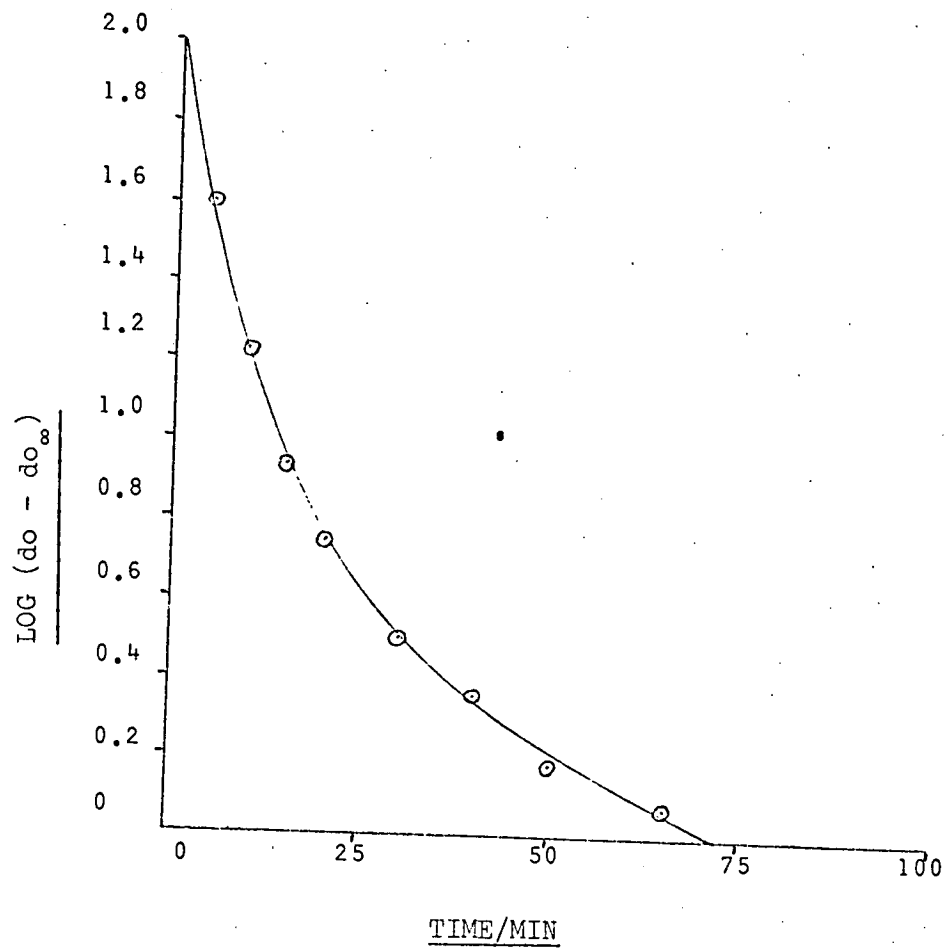


Figure 5.6. First Order Rate Plot (ko) For Propylene/D₂O Exchange on D₂O pretreated 9.09 Atom % Sb Catalyst at 473 K.

Table 5.3 shows a comparison between the initial first order rate constants $k\phi$ and k_0 for the 9.09 atom % Sb catalyst at 473 K used for reaction following:-

- (1) No pretreatment. (i.e. catalyst only outgassed).
- (2) Propylene pretreatment.
- (3) D_2O pretreatment.

It should be noted that during the course of runs in which the catalyst had been pretreated with D_2O , the loss of propylene from the gas phase was almost negligible, being typically about 5% after 5 hours.

5.3.2. Heavy Water Pretreatment.

As has just been shown, pretreatment of a catalyst with D_2O prior to a run, resulted in an increase in the initial rate of exchange. It could be that this increase in the initial rate of exchange is attributable to replacement of some surface hydroxyl groups by deuterioxyl groups during the pretreatment process. If this were so, then by monitoring an exchange reaction with propylene as the only reactant, over a previously D_2O pretreated catalyst, then an estimate of the number of active $-OD$ sites generated on the catalyst surface, by the pretreatment process, could be obtained.

Experimental.

The experimental procedure was similar to that described previously for D_2O pretreatment, the only departure being that after the D_2O had been pumped off for 10 minutes, propylene 0.53 k Nm^{-2} (4 mm Hg) was admitted to the reaction vessel and the exchange reaction was followed by the usual technique, at 473 K.

Treatment of Results.

As an approximation each oxygen atom was regarded as being capable of conversion to a deuteroyl group during the pretreatment process. Now, by assuming that 1 m^2 of surface contains 6×10^{18} oxygen atoms, regardless of crystallographic structure and the exact representation of the surface⁽⁸⁷⁾, then we can calculate the maximum possible number of active sites from the surface area of the catalyst. Thus, for the 6.13 atom % Sb catalyst with a surface area of $12.2 \text{ m}^2 \text{ g}^{-1}$ we have $6 \times 10^{18} \times 12.2 = 7.32 \times 10^{19}$ active sites on 1 g of catalyst. The total number of molecules of propylene in the reaction vessel = 1.60×10^{19} .

Each productive visit of a propylene molecule to the catalyst surface results in one active deuteroyl site being used up. The number of sites consumed at any given time may be calculated from the exchange data by assuming that equilibration between surface species and the gas phase readily occurs and that there is no kinetic isotope effect.

Results.

The results obtained on the 6.13 atom % Sb and the 9.09 atom % Sb catalysts are given in tables 5.4 and 5.5 and are illustrated graphically in Figure 5.7.



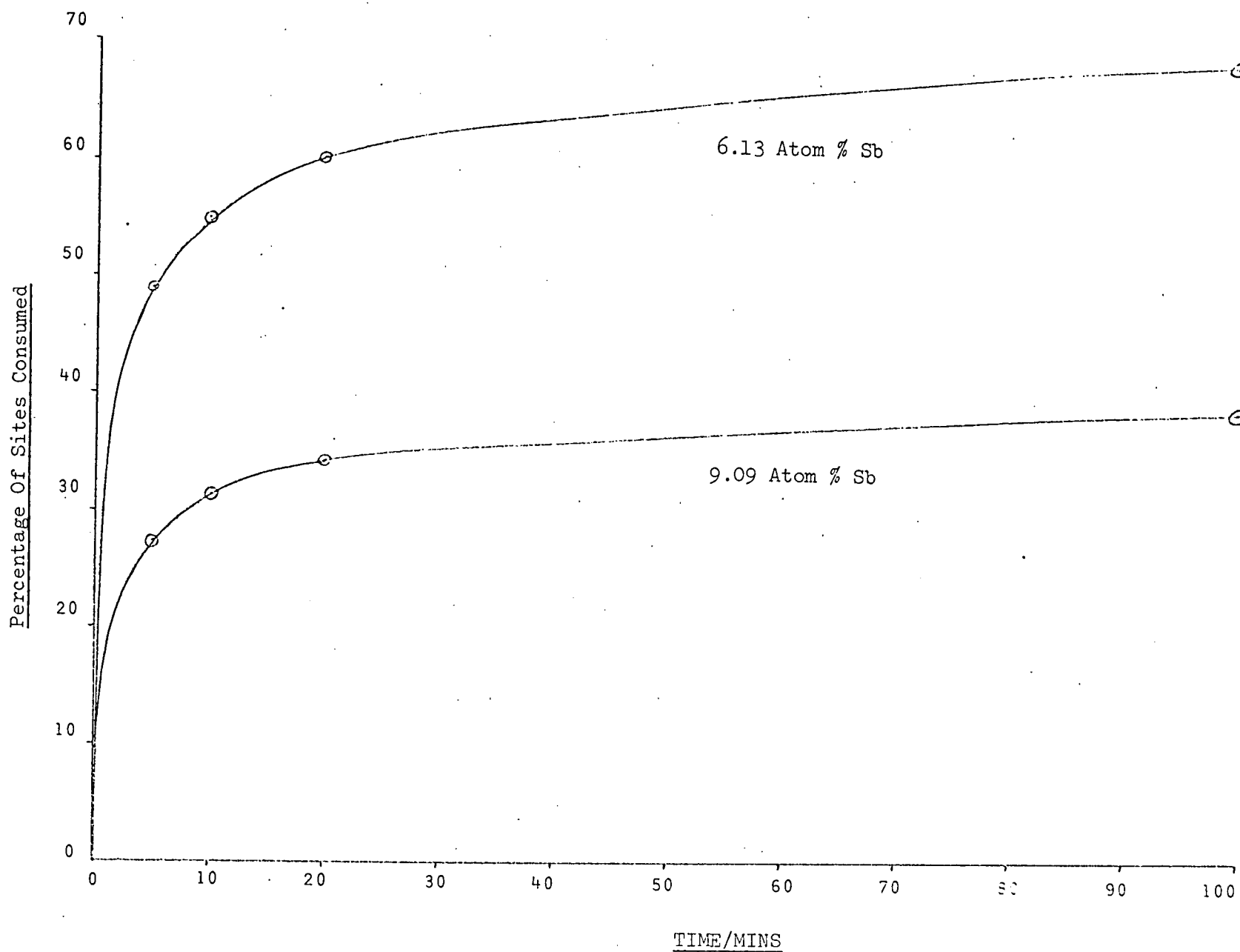


Figure 5.7 Percentage Of Sites Consumed During Propylene Exchange on D_2O Pretreated 6.13 and 9.09 Atom % Sb Catalysts at 473 K.

Percentage of Active Deuteroyl Sites Consumed during Propylene ExchangeTABLE 5.4

6.13 atom % Sb catalyst

Time (Min)	% of Sites Consumed
0	0
5	49.0
10	55.2
20	60.0
100	67.8

TABLE 5.5

9.09 atom % Sb catalyst

Time (Min)	% of Sites Consumed
0	0
5	27.4
10	31.4
20	34.2
100	38.4

5.3.3. Catalytic Activity in Relation to Catalyst Composition.

The propylene/D₂O exchange reaction was effectively catalysed by the range of tin-antimony-oxide catalysts studied. However, the initial rate of the exchange reactions varied depending on the catalyst composition. If the initial rate constant k_0 is taken as a measure of the catalytic activity, at a constant temperature of 473 K, then we may plot catalyst activity against atom % Sb i.e. against % composition of the catalyst, as shown in Figure 5.8. A similar result can be obtained if the plot of $k\phi$ against atom % Sb is constructed. A plot of the specific reaction rate constant, (i.e. the first order rate constant corrected for catalyst weight and surface area), is shown in Figure 5.9, and in effect nullifies the catalytic influence of surface area. A summary of the results obtained for the propylene/D₂O exchange reactions, on a number of catalysts, is shown in Table 5.6.

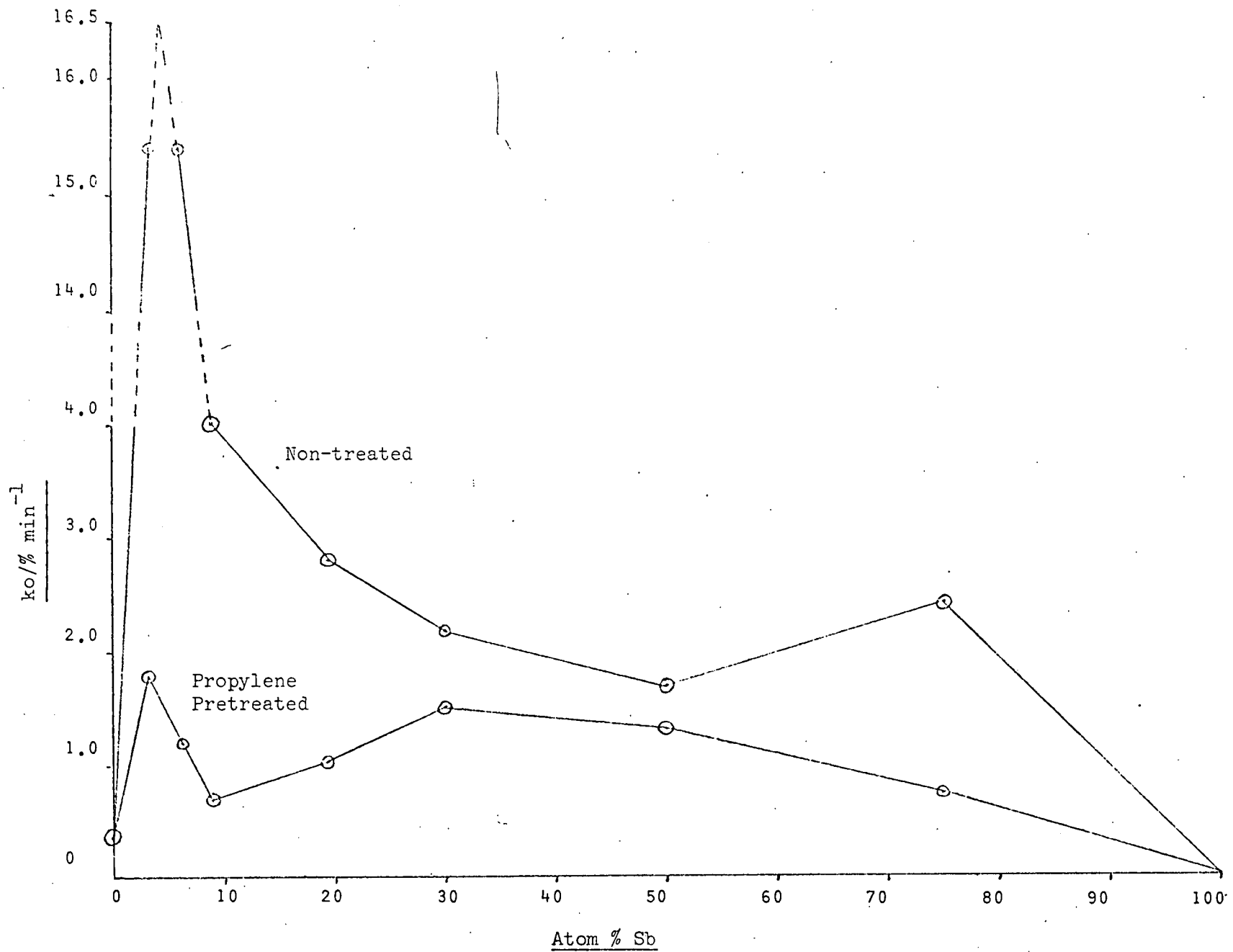


Figure 5.8 Catalytic Activity As A Function Of Catalyst Composition For Propylene/D₂O Exchange At 473 K.

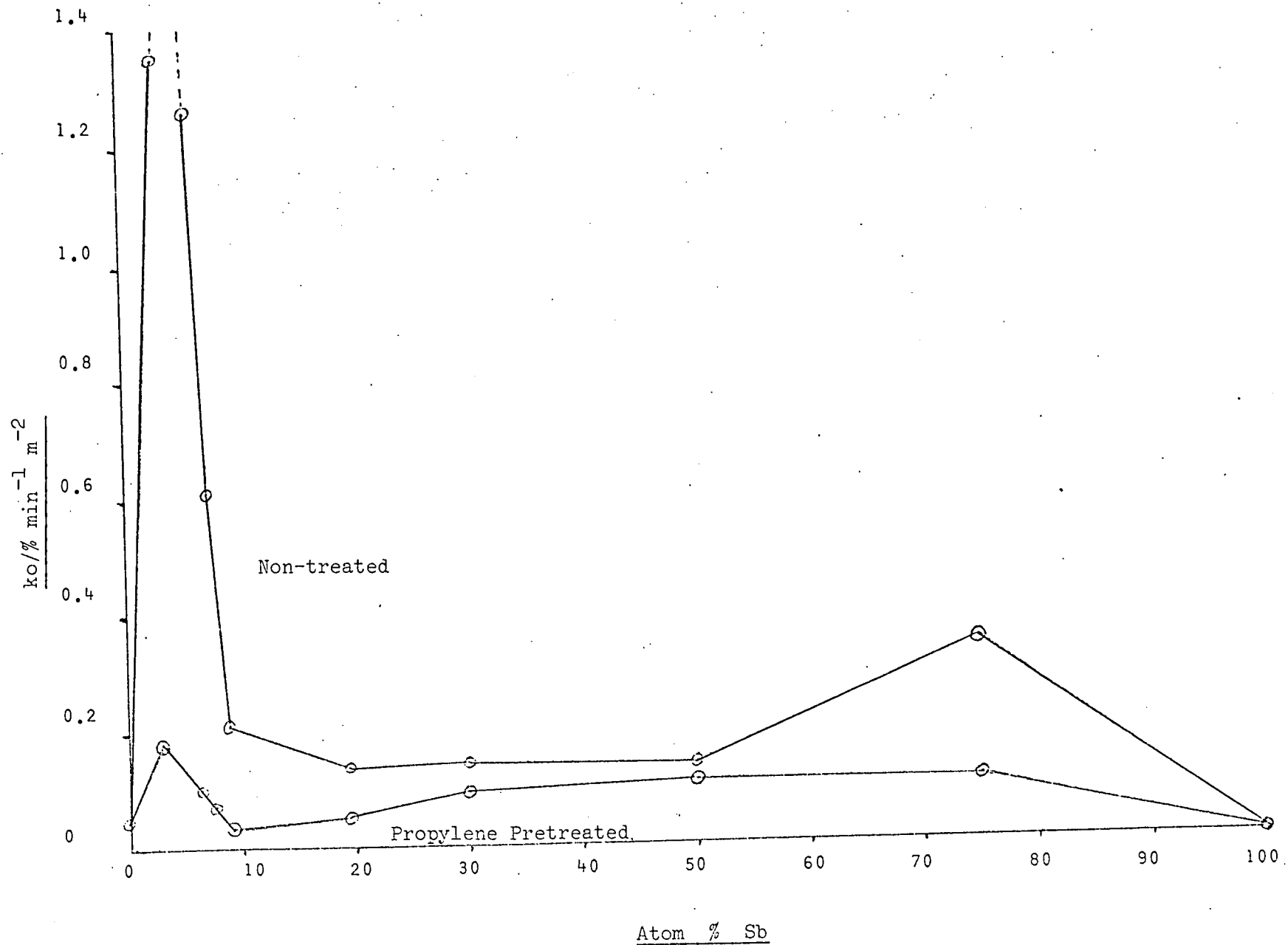


Figure 5.9 Specific Catalytic Activity As A Function Of Catalyst Composition For Propylene/ D_2O Exchange At 473 K.

PROPYLENE/D₂O EXCHANGE REACTIONS.

Catalyst Composition Atom % Antimony	Temperature K	Propylene Treatment of Catalyst	$k\phi$ *	k_0 % min ⁻¹	Specific $k\phi \times 10$ * m ⁻²	Specific $k_0 \times 10$ % min ⁻¹ m ⁻²	M Value
0.00	473	non-treated	0.17	0.18	0.40	0.43	0.94
0.00	473	pre- "	0.24	0.24	0.57	0.57	1.00
3.30	473	non- "	16.25	15.40	16.41	13.50	1.05
3.30	473	pre- "	1.80	1.80	1.82	1.82	1.00
6.13	473	non- "	15.50	15.40	12.70	12.62	1.01
6.13	473	pre- "	1.27	1.20	1.04	0.98	1.05
7.40	473	non- "	14.02	11.00	7.75	6.08	1.27
7.40	473	pre- "	1.37	1.27	0.76	0.71	1.08
9.09	473	non- "	4.93	4.02	2.57	2.10	1.23
9.09	473	pre- "	0.72	0.69	0.37	0.36	1.04
19.60	473	non- "	2.83	2.80	1.36	1.35	1.00
19.60	473	pre- "	1.20	1.03	0.57	0.50	1.15
29.60	473	non- "	2.73	2.17	1.78	1.41	1.25
29.60	473	pre- "	1.89	1.50	1.23	0.98	1.25
49.50	473	non- "	2.31	1.67	1.85	1.34	1.38
49.50	473	pre- "	1.50	1.30	1.20	1.04	1.19
75.00	473	non- "	3.11	2.42	4.44	3.46	1.28
75.00	473	pre- "	0.90	0.73	1.29	1.05	1.23
100.00	473	non- "	} Rates	Less by a	Factor of \approx	10 ²	
100.00	473	pre- "					

* Footnote:- $k\phi$ value is equivalent to the number of deuterium atoms entering 100 molecules of hydrocarbon in unit time.

A summary of the results obtained so far is as follows:-

- (1) Only 5 of the 6 propylene hydrogen atoms are exchangeable.
- (2) The exchange occurs in a stepwise manner.
- (3) The activity of non-treated catalysts decreases with time, an effect which is paralleled by a marked loss of propylene from the gas phase.
- (4) Catalysts pretreated with propylene exhibit steady activity and obey first order kinetics.
- (5) Catalysts pretreated with D_2O exhibit an enhanced initial rate of exchange, an effect which is paralleled by a marked reduction in the loss of propylene from the gas phase.
- (6) D_2O pretreatment of the catalyst followed by a run using propylene as the only reactant, resulted in an estimation of the number of active sites on the catalyst surface.
- (7) A plot of catalytic activity against % composition of the catalysts, indicated that the non-treated catalysts around 5 atom % Sb were extremely active.

The evidence from observations (1) and (2), combined with support from the literature, could suggest that the hydrogen atom, bonded to the central carbon atom of the propylene molecule, is the hydrogen atom least likely to undergo exchange. The evidence also suggests that the exchange reaction could occur via a carbanion, carbonium ion or allylic type of intermediate. However, the most likely intermediates would be either carbonium ion or allylic types⁽⁶⁶⁾.

In order to obtain further clarification of the mechanism by which the exchange reaction proceeds, the reaction between isobutene and heavy water was investigated over the complete range of catalysts.

5.3.4. Isobutene/D₂O Exchange.

If the exchange reaction proceeds via a carbonium ion type of intermediate, then we would expect the rate of the exchange reaction to be considerably faster for isobutene than for propylene, due to the formation of a tertiary carbonium ion⁽⁸⁸⁾. If, however, the exchange reaction proceeds via an allylic type of intermediate, then we would expect the exchange reaction to occur at a somewhat similar rate, for both isobutene and propylene⁽⁶⁶⁾.

Experimental.

The experimental conditions and procedures were basically as described for propylene. Runs on fresh 1 g samples of the same series of catalysts, both non-treated and pretreated with isobutene (0.53 k Nm⁻² (4mm Hg)(60 min)), have been carried out. The reaction mixture consisted of isobutene and heavy water in the mole ratio of 1:4, total pressure in the reaction vessel being 1.20 k Nm⁻² (9 mm Hg). Initially a reaction temperature of 473 K was employed. However, for most catalysts the rate of exchange at 473 K was too rapid for accurate measurement and a temperature of 323 K was finally employed. * Footnote.

Results.

First order rate plots for the disappearance of the light isobutene and for the appearance of the heavy isobutene, were linear for

* The author wishes to thank Mr. A.G. Myles for his assistance with the experimental work.

catalysts pretreated with isobutene, and curved for non-treated catalysts, (typical examples being shown in Figures 5.10 and 5.11). The initial rate constants $k\phi$ and k_0 were obtained by considering the initial portions of the plots, over a period of approximately 60 minutes.

The percentage distribution of isomers plotted against time, clearly indicated that all the eight isobutene hydrogen atoms undergo exchange as shown in Figure 5.12. Furthermore, comparison of the experimental distributions obtained after discrete extents of reaction, with the theoretically calculated distributions for stepwise exchange of a molecule containing eight equally reactive hydrogen atoms, showed that all eight hydrogen atoms react at the same rate, (typical results being shown in Table 5.7).

TABLE 5.7

Calculated and Experimental Distributions of Isobutenes.

	percentage of isotopic species									ϕ
	d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	
Experimental *	0.3	3.5	11.7	22.5	27.2	21.3	10.2	2.8	0.4	394.0
Calculated	0.4	3.4	11.6	22.5	27.3	21.2	10.3	2.9	0.3	394.0

* After reaction on 29.60 atom % Sb catalyst for
140 mins. at 323 K.

The value of ϕ indicates the extent of the exchange reaction.

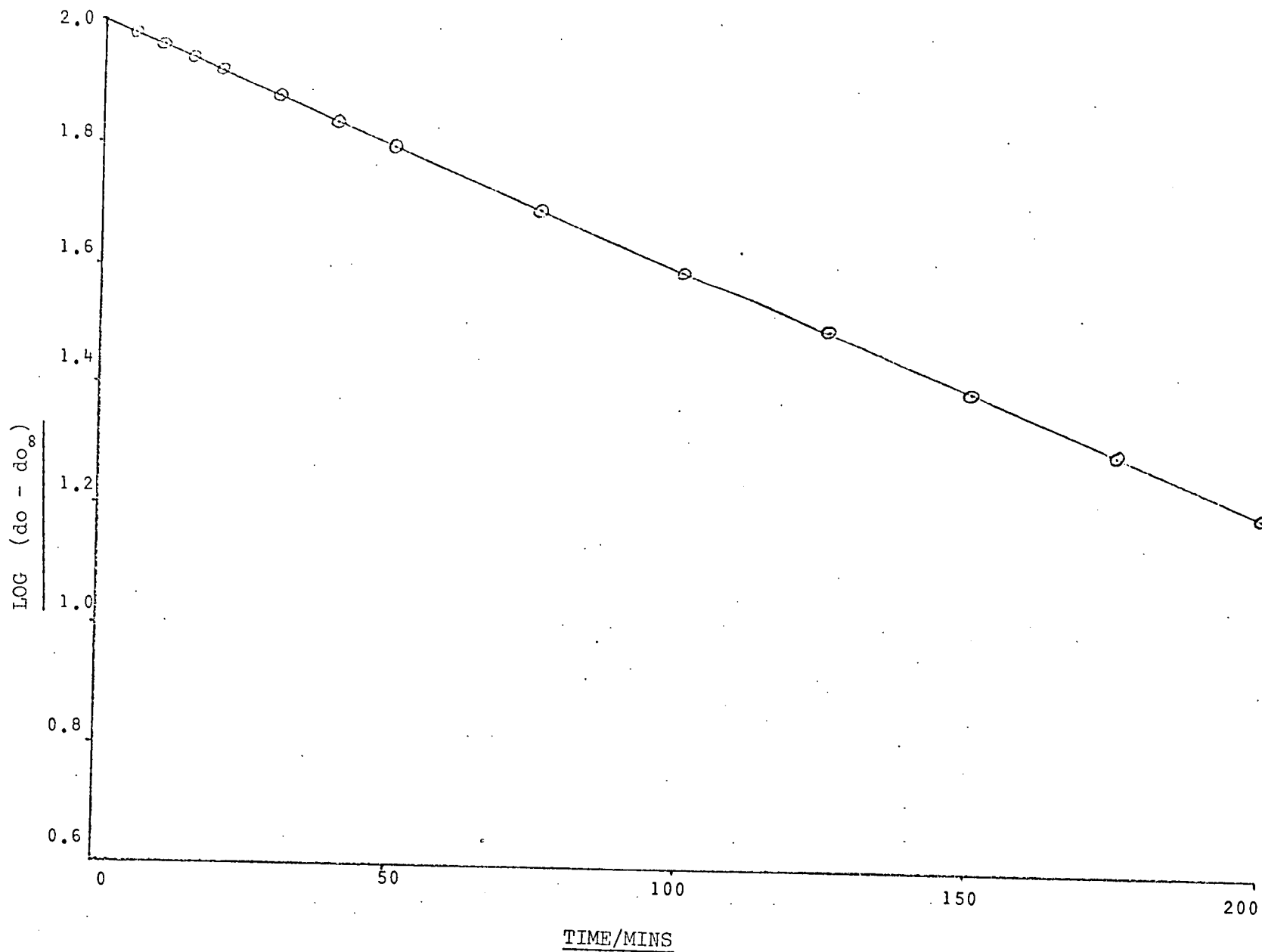


Figure 5.10 First Order Rate Plot (ko) For Isobutene/D₂O Exchange On Isobutene Pretreated 29.60 Atom % Sb Catalyst at 323 K.

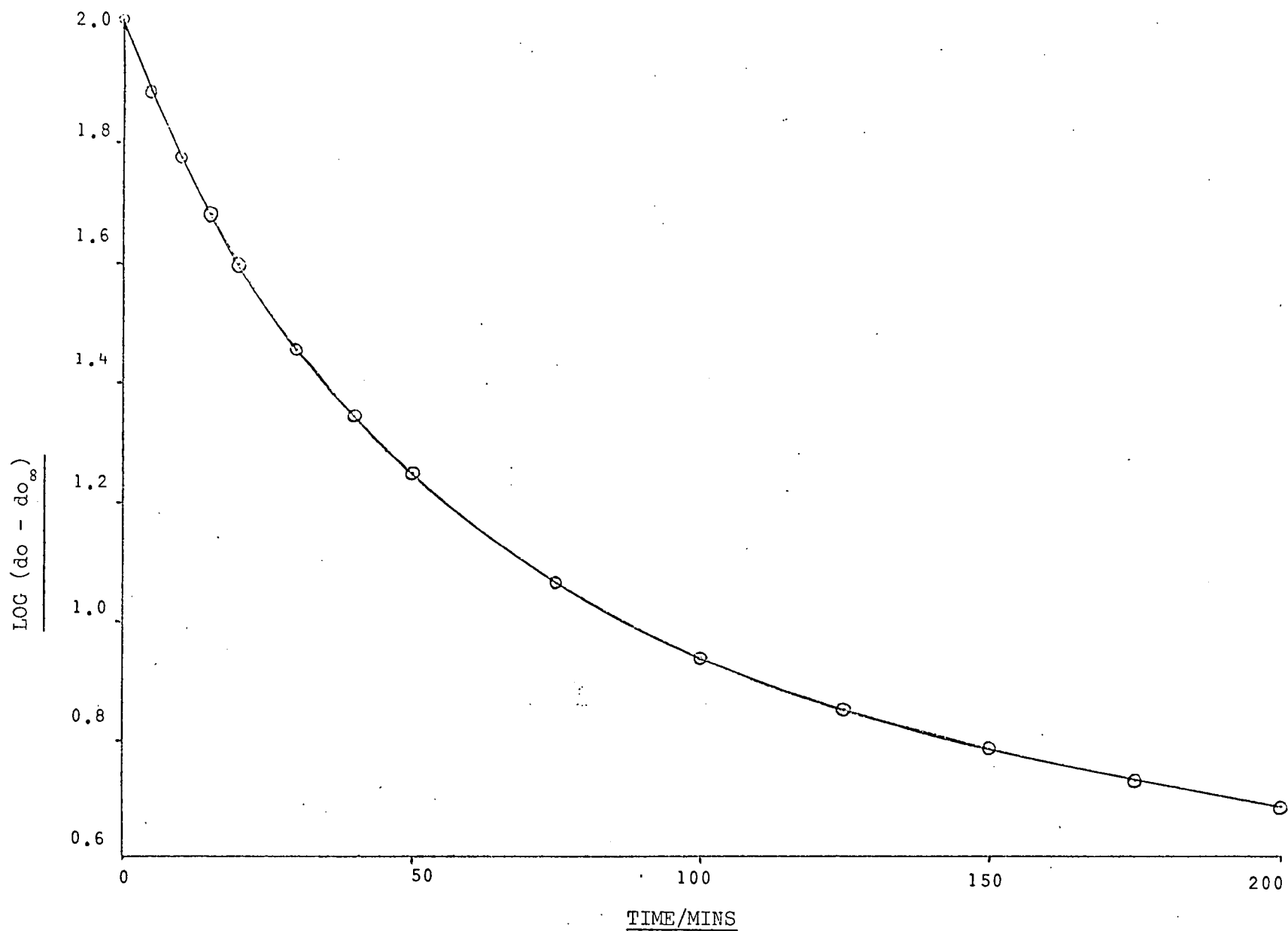


Figure 5.11 First Order Rate Plot (ko) For Isobutene/D₂O Exchange On Non-treated 29.60 Atom % Sb Catalyst At 323 K.

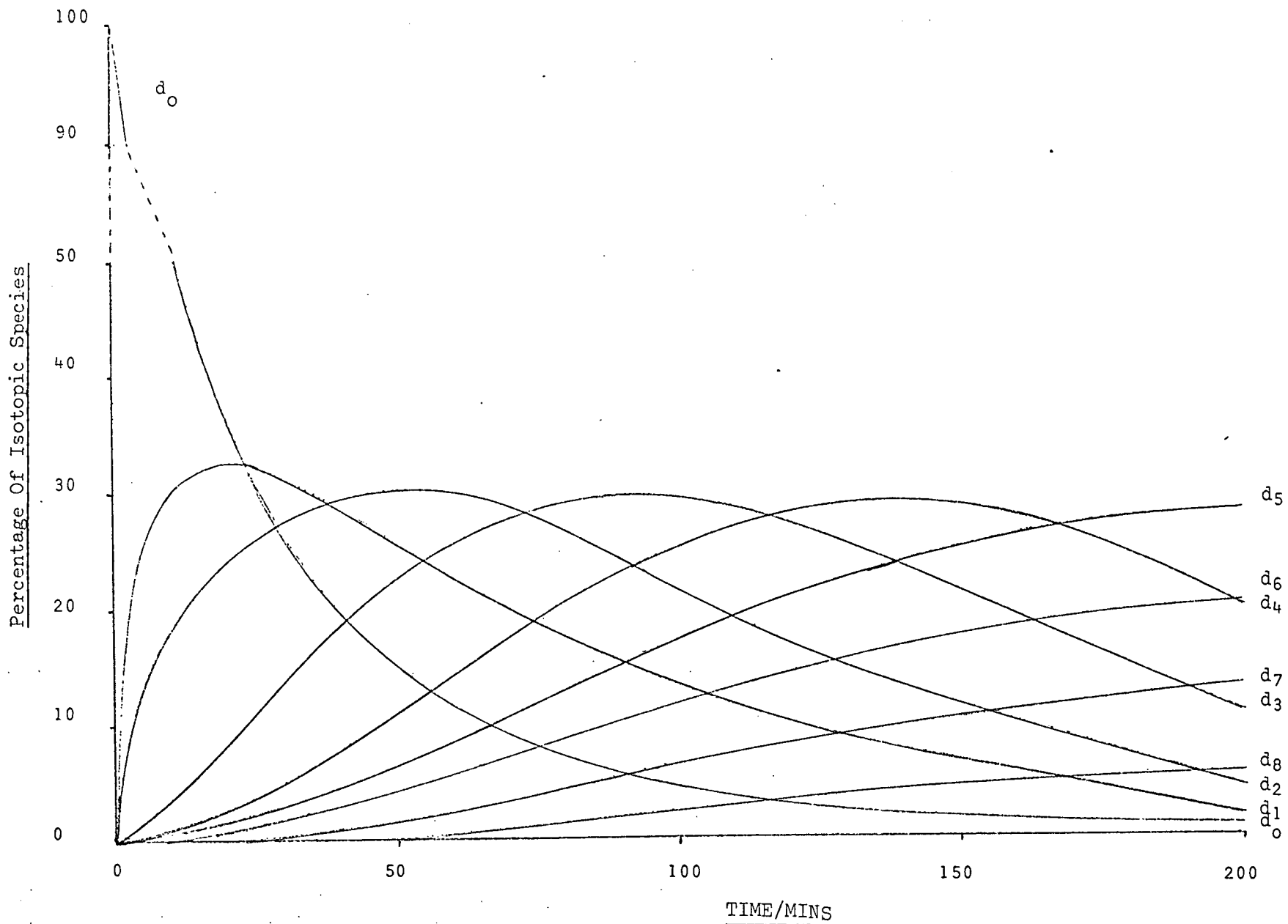


Figure 5.12 Distribution Of Isomers For Isobutene/D₂O Exchange On Non-treated 29.60 Atom % Sb Catalyst at 323 K.

Isotopic product distribution closely followed the calculated binomial distribution, as shown in Table 5.7, and this fact, in conjunction with an M value of about one, supported a simple or stepwise exchange mechanism. During runs on non-treated catalysts the total isotopic isobutene peak height decreased substantially with time, in extreme cases being approximately 50% after 5 hours, indicating loss of isobutene from the gas phase. This effect was considerably reduced in the case of an isobutene pretreated catalyst, the loss being typically 15-20% over 5 hours.

Runs on fresh 1 g samples of 9.09 atom % Sb catalysts, pretreated with isobutene, were carried out at a number of temperatures in order to obtain the relevant Arrhenius parameters. Table 5.8 summarises the specific reaction rate constants and M values, obtained at the different temperatures.

ISOBUTENE/D₂O EXCHANGE REACTIONS

Catalyst Composition Atom % Antimony	Temperature K	Isobutene Treatment of Catalyst	$k\phi$ *	k_o % min ⁻¹	Specific $k\phi \times 10$ * m ⁻²	Specific $k_o \times 10$ % min ⁻¹ m ⁻²	M Value	
0.00	473	non-treated	4.36	4.34	10.38	10.33	1.00	
0.00	473	pre- "	1.15	1.17	2.74	2.78	0.98	
6.13	323	non- "	8.65	8.40	7.09	6.88	1.03	
6.13	323	pre- "	6.79	6.06	5.56	4.97	1.12	
9.09	323	non- "	9.11	9.20	4.74	4.79	0.99	
9.09	323	pre- "	6.84	5.90	3.56	3.07	1.16	
9.09	348	non- "	21.60	20.00	11.25	10.42	1.08	
9.09	348	pre- "	14.39	11.99	7.49	6.25	1.20	
9.09	373	non- "	62.18	57.57	32.38	29.98	1.08	
9.09	373	pre- "	22.12	18.43	11.52	9.60	1.20	
29.60	323	non- "	4.94	4.88	3.21	3.17	1.01	
29.60	323	pre- "	0.87	0.89	0.56	0.58	0.98	
49.50	323	non- "	4.65	4.47	3.72	3.57	1.04	
49.50	323	pre- "	1.41	1.37	1.13	1.09	1.02	
75.00	323	non- "	1.05	0.93	1.50	1.33	1.19	
75.00	323	pre- "	0.84	0.72	1.20	1.03	1.16	
100.00	473	non- "	0.40	0.29	4.45	3.22	1.35	
100.00	473	pre- ")	Rates Less by a Factor of ≈ 30 .					

* The $k\phi$ value is equivalent to the number of deuterium atoms entering 100 molecules of hydrocarbon in unit time.

An Arrhenius plot was constructed by plotting $\log k_0$ against K/T as shown in Figure 5.13 and from this the activation energy was found to be $23.44 \text{ kJ mole}^{-1}$. The Arrhenius parameters obtained from the plot correspond to the equation

$$r_0 = 10^{18.45} e^{-23.44/RT}$$

where r_0 is the absolute rate in molecules $\text{sec}^{-1} \text{ m}^{-2}$ and the activation energy is given in kJ mole^{-1} .

Comparison of the initial rates of exchange for the propylene/ D_2O and the isobutene/ D_2O exchange reactions over the 9.09 atom % Sb pretreated catalysts can be obtained by extrapolation of the relevant Arrhenius plot data. This has been carried out graphically and is shown in Figure 5.14. The results indicate that:-

at 323 K the rate of isobutene/ D_2O exchange is faster than the rate of propylene/ D_2O exchange by a factor of 450.

at 373 K the rate of isobutene/ D_2O exchange is faster than the rate of propylene/ D_2O exchange by a factor of 275.

at 473 K the rate of isobutene/ D_2O exchange is faster than the rate of propylene/ D_2O exchange by a factor of 140.

All the catalysts including antimony oxide were found to catalyse the isobutene/ D_2O exchange reaction and all gave rise to the characteristic kinetics as discussed previously. However, as for propylene, the initial rate constants varied throughout the catalyst range, being dependent on catalyst composition. If the initial rate constant k_0 is taken as a measure of the catalyst activity at a constant temperature of 323 K, then

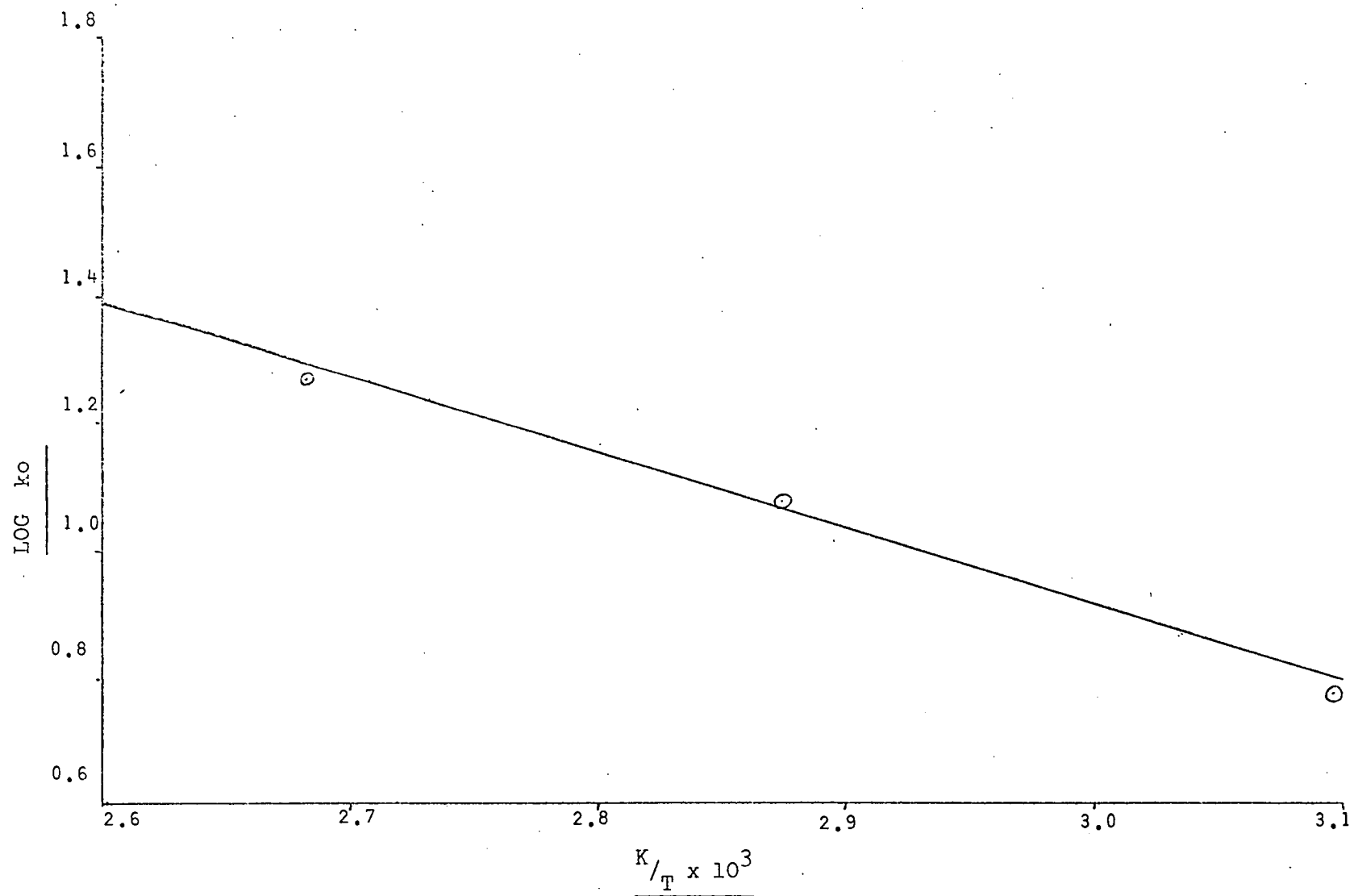


Figure 5.13 Arrhenius Plot For Isobutene/D₂O Exchange On Isobutene Pretreated 9.09 Atom % Sb Catalyst.

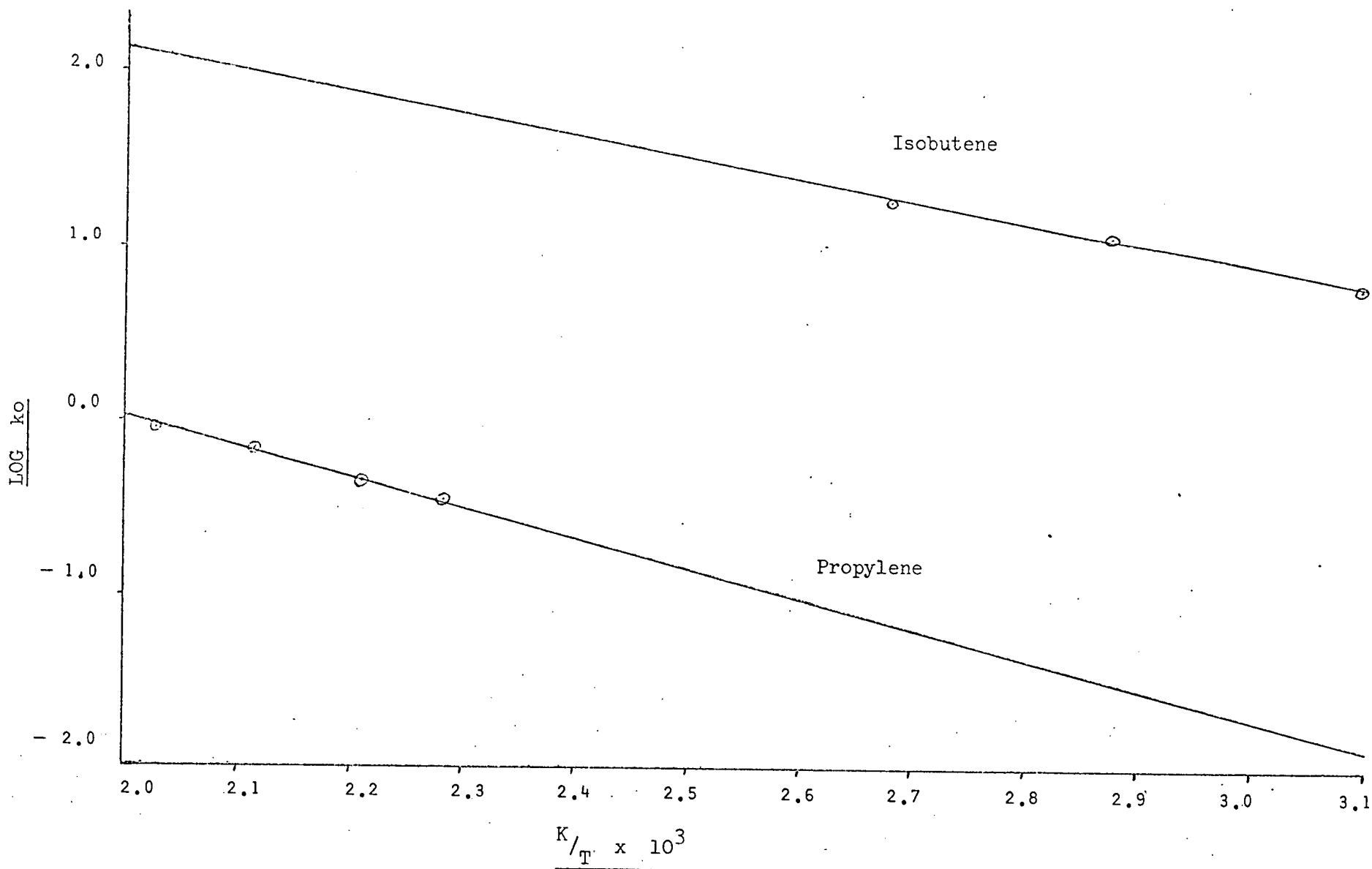


Figure 5.14 Extrapolated Arrhenius Plots For Propylene/D₂O And Isobutene/D₂O Exchange On Pretreated 9.09 Atom % Sb Catalysts.

a plot of catalytic activity against % catalyst composition can be constructed as shown in Figures 5.15 and 5.16. A similar result can be obtained by the use of the $k\phi$ value. A summary of the results for isobutene/ D_2O exchange is shown in Table 5.8. Comparison of the results for isobutene, in Table 5.8, with those for propylene, in Table 5.6, indicates that, although the reaction temperature is lower by 150 K, the k_0 and $k\phi$ values for isobutene are greater than the corresponding values for propylene.

A summary of the results obtained for the isobutene/ D_2O exchange reaction is given below:-

- (1) All 8 of the isobutene hydrogen atoms undergo exchange.
- (2) The exchange occurs in a stepwise manner.
- (3) The activity of non-treated catalysts diminishes with time, an effect which is paralleled by a marked loss of isobutene from the gas phase.
- (4) Catalysts pretreated with isobutene exhibit steady activity and result in first order kinetics.
- (5) A plot of catalytic activity against % composition of the catalyst, indicated that maximum catalytic activity was to be found around the 5 atom % Sb region.
- (6) Comparison of the initial rates of exchange for the propylene/ D_2O and isobutene/ D_2O exchange reactions indicated that the isobutene/ D_2O exchange reaction was considerably faster.

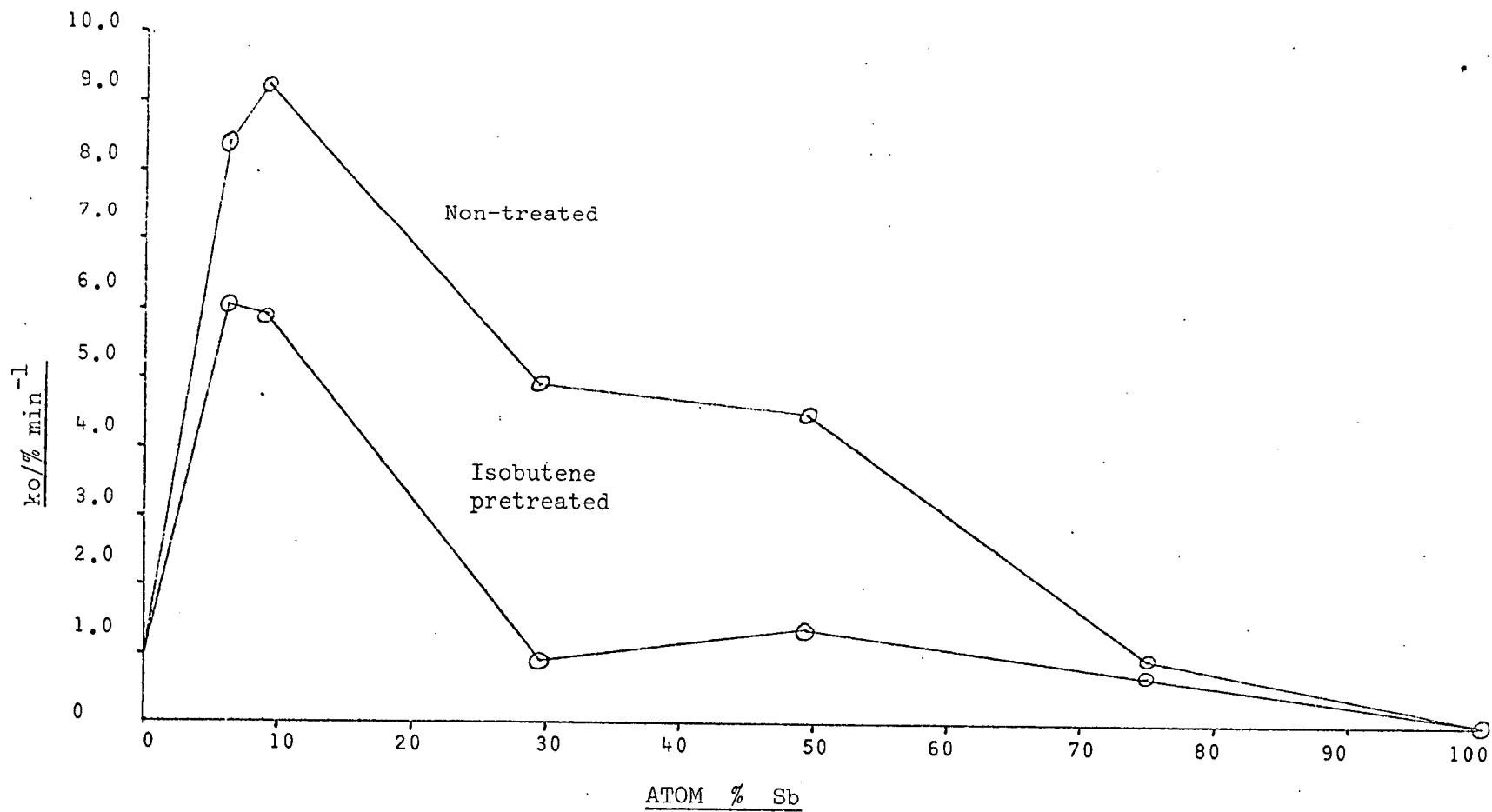


Figure 5.15 Catalytic Activity As A Function Of Catalyst Composition For Isobutene/ D_2O Exchange At 323 K.

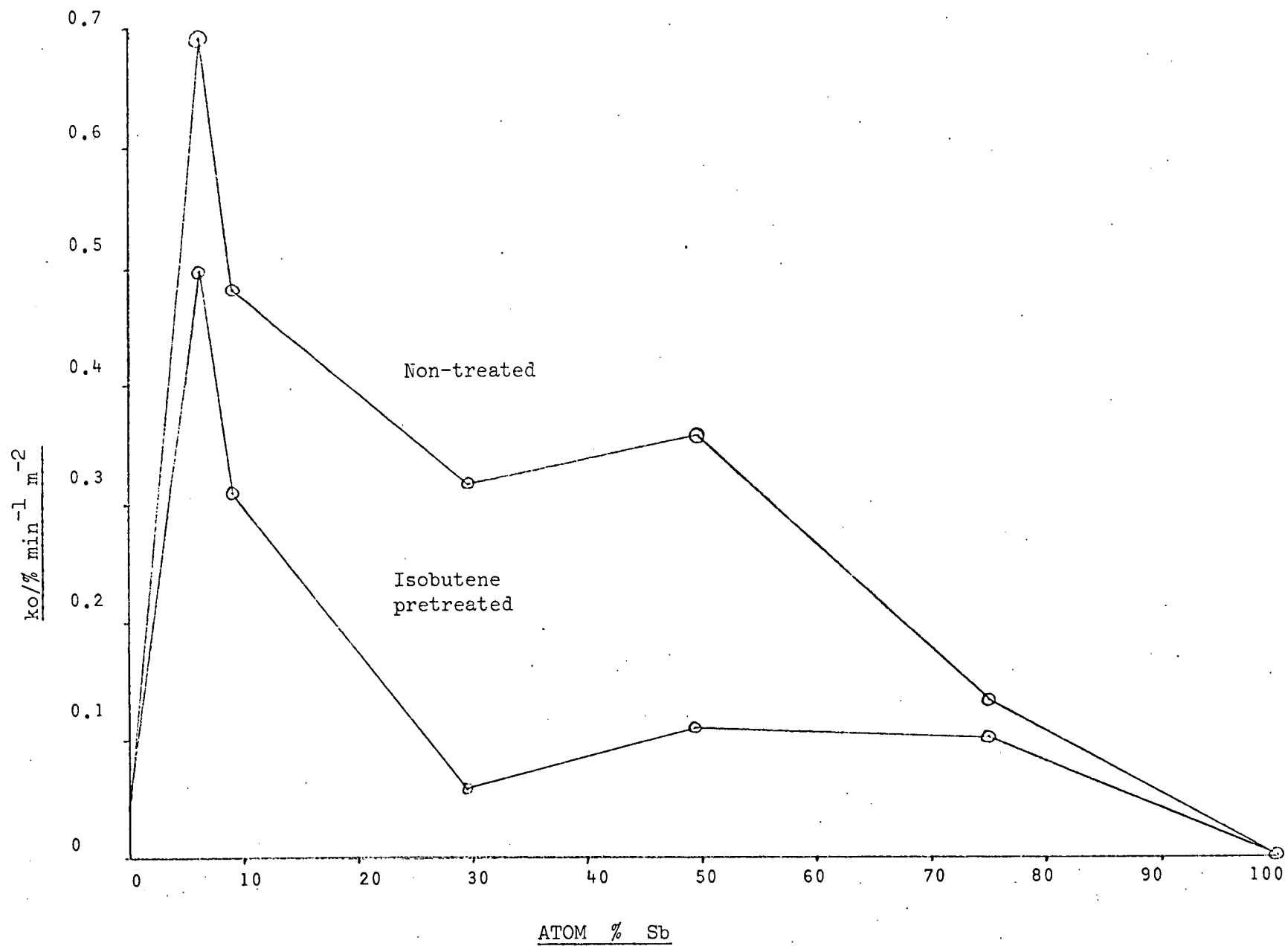


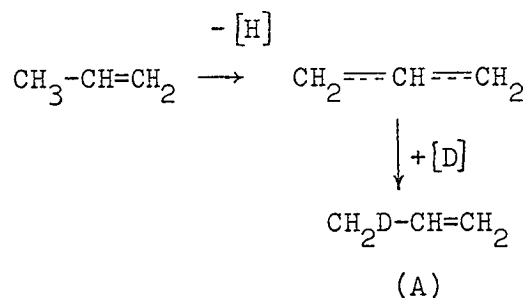
Figure 5.16 Specific Catalytic Activity As A Function Of Catalyst Composition For Isobutene/D₂O Exchange At 323 K.

5.3.5. Infrared Spectroscopic Analysis of Reaction Products.

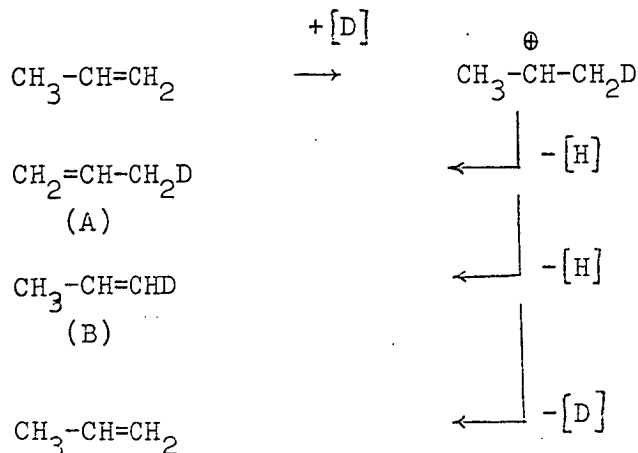
The results from the isobutene/D₂O exchange reactions could indicate, that the exchange is more likely to occur via a carbonium ion type intermediate than an allylic type. However, this does not mean to say that propylene/D₂O exchange must also occur via a carbonium ion type of intermediate. In order to clarify the situation with regard to propylene/D₂O exchange, infrared analysis of the reaction products was employed to determine the nature of the active intermediate (111).

Consider now the hydrogen-deuterium exchange reaction between propylene and D₂O, involving the following intermediates:-

(1) Allylic intermediate



(2) Carbonium Ion intermediate



Products (A) and (B) can be identified by infrared spectroscopic analysis.

The mechanistic scheme above indicates that if the propylene/ D_2O exchange reaction proceeds via an allylic type of intermediate, then only one monodeuterated product should be obtained, namely the 1-propene- $3d_1$. If, on the other hand, the exchange proceeds via a carbonium ion type of intermediate then two monodeuterated products should be obtained, namely the 1-propene- $3d_1$ and the 1-propene- $1d_1$. It is fundamentally important to ensure that the d_1 stage of the exchange reaction is not exceeded.

Experimental.

The bands chosen for the infrared spectroscopic analysis were the $\begin{matrix} \text{H} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{D} \end{matrix}$ wag frequency at 799 cm^{-1} for $CH_3-CH=CHD$, and the methyl C-D stretch frequency at 2169 cm^{-1} for $CH_2D-CH=CH_2$. The choice of bands was based on a survey of the available literature (89,90 and 91) and on the infrared spectra of reference samples of the two monodeuterated propenes, determined on the same instrument as the actual product analysis, (see i.r. spectra nos. 1, 2 and 3). The 2169 cm^{-1} band was found to be considerably weaker than the 799 cm^{-1} band for similar pressures of the two propenes. It may be noted that for $CHD=CH-CH_3$ both cis and trans forms exist and although the cis form at 799 cm^{-1} may be expected to be greater, the trans form at 975 cm^{-1} was also monitored.

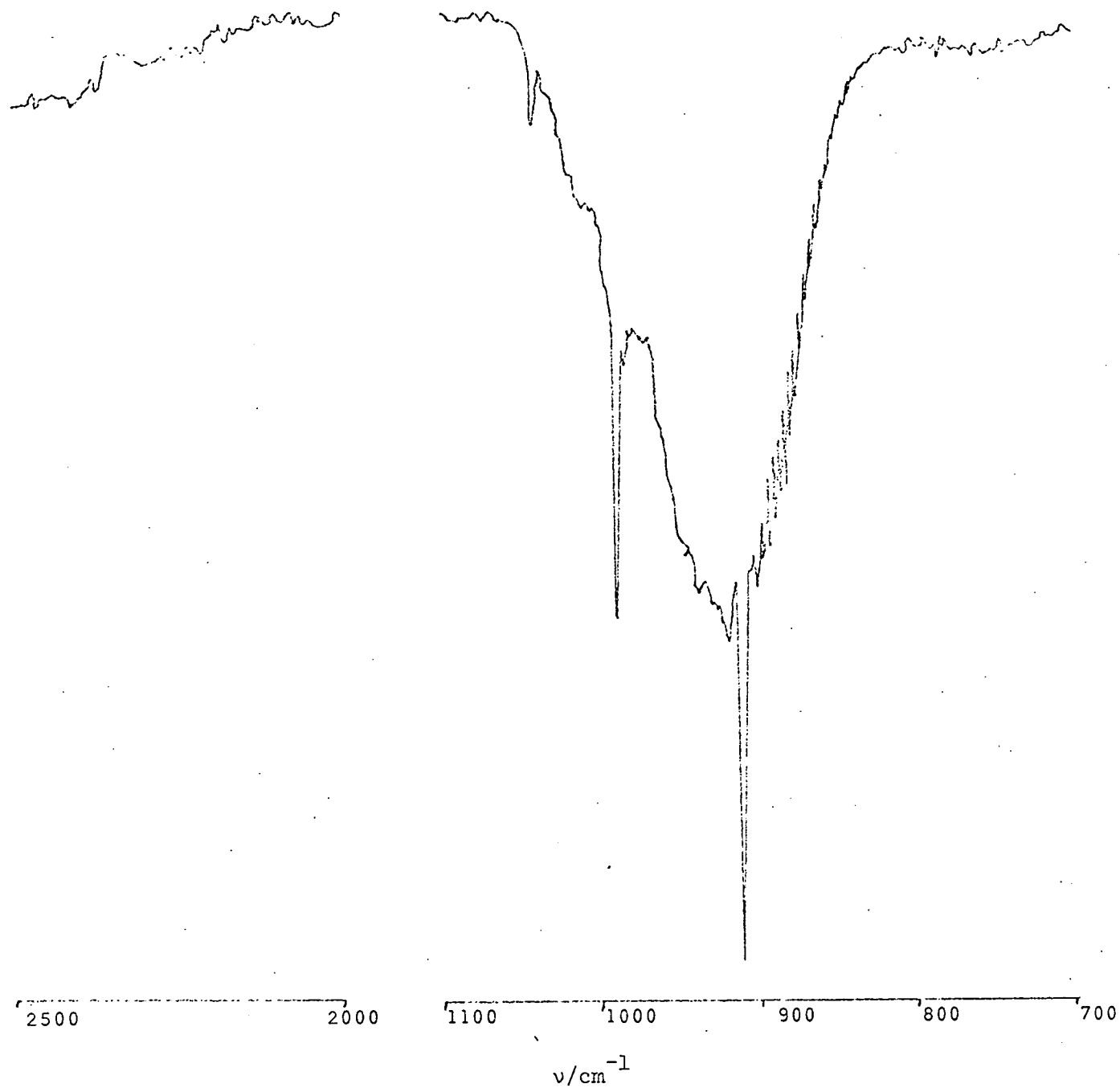
Experimentally the conditions were basically similar to those for a normal run. The catalyst used was 29.6 atom % Sb oxide pretreated with propylene and the reactants were propylene: D_2O in a ratio of 1:1. The reaction was carried out at a low temperature which allowed the progress of the reaction to be monitored, in detail, by the mass spectrometric technique.

During the course of a run, the point corresponding to the maximum amount of the d_1 species, prior to any build up of d_2 , could be monitored accurately by the mass spectrometer. At that point all the gaseous reactants and products were condensed rapidly into a 10 cm path-length infrared gas cell. The procedures of admitting the reactant gases, reaction, then condensation were repeated several times until a pressure of approximately 6.67 k Nm^{-2} (50 mm Hg) was obtained in the gas cell. The infrared spectra were then run on a Perkin-Elmer 225 spectrometer.

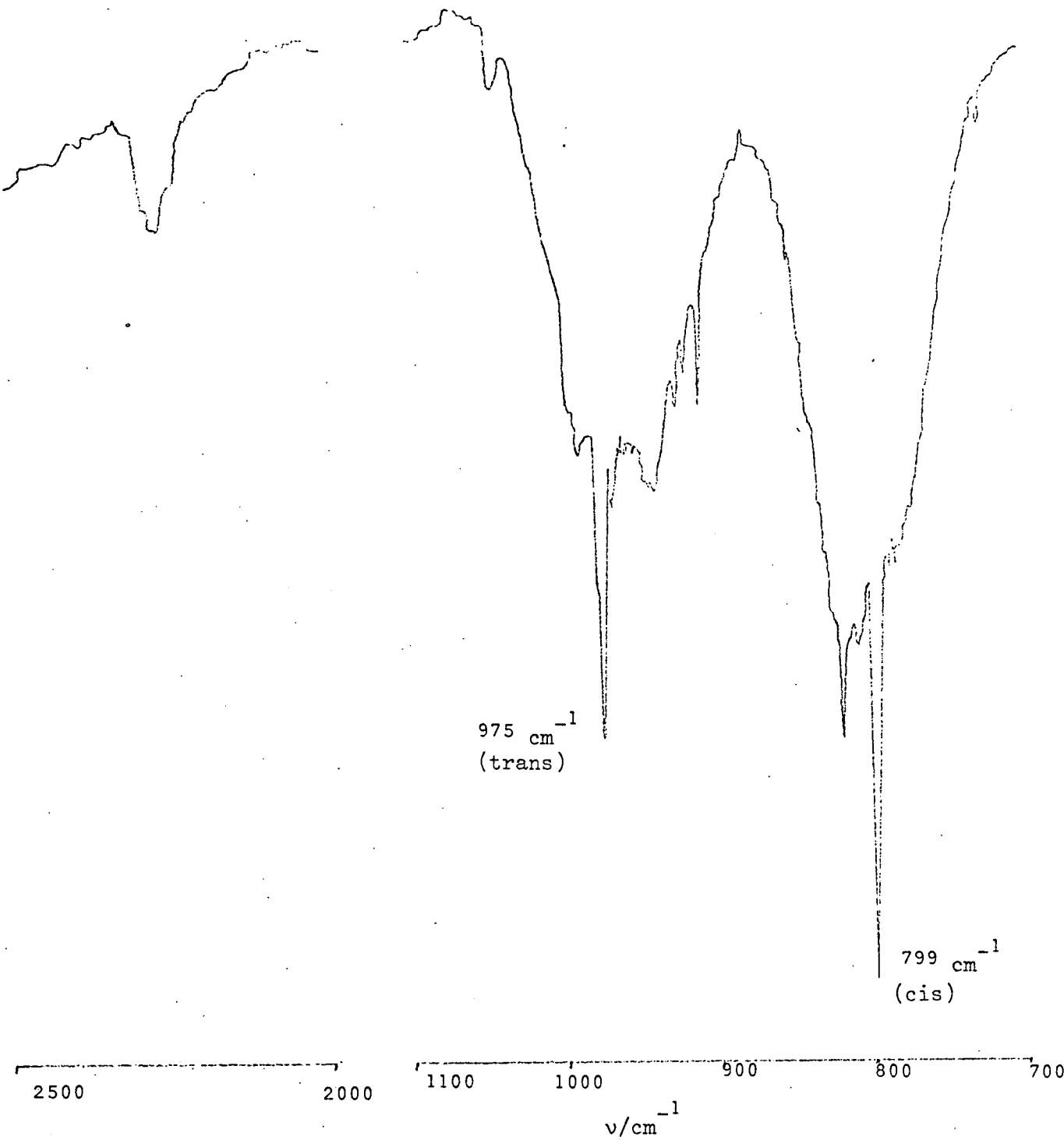
Results.

The infrared spectra of the reaction products showed an absorption of medium intensity at 2169 cm^{-1} and an extremely weak absorption at 799 cm^{-1} as shown in i.r. spectra no. 4. These absorptions are in good agreement with the corresponding absorptions from the monodeuterated reference samples. The results indicated quite clearly that only one monodeuterated product, namely the 1-propene- $3d_1$, was produced. Therefore, one must conclude that propylene/ D_2O exchange over tin-antimony-oxide catalysts proceeds almost entirely via an allylic type of intermediate.

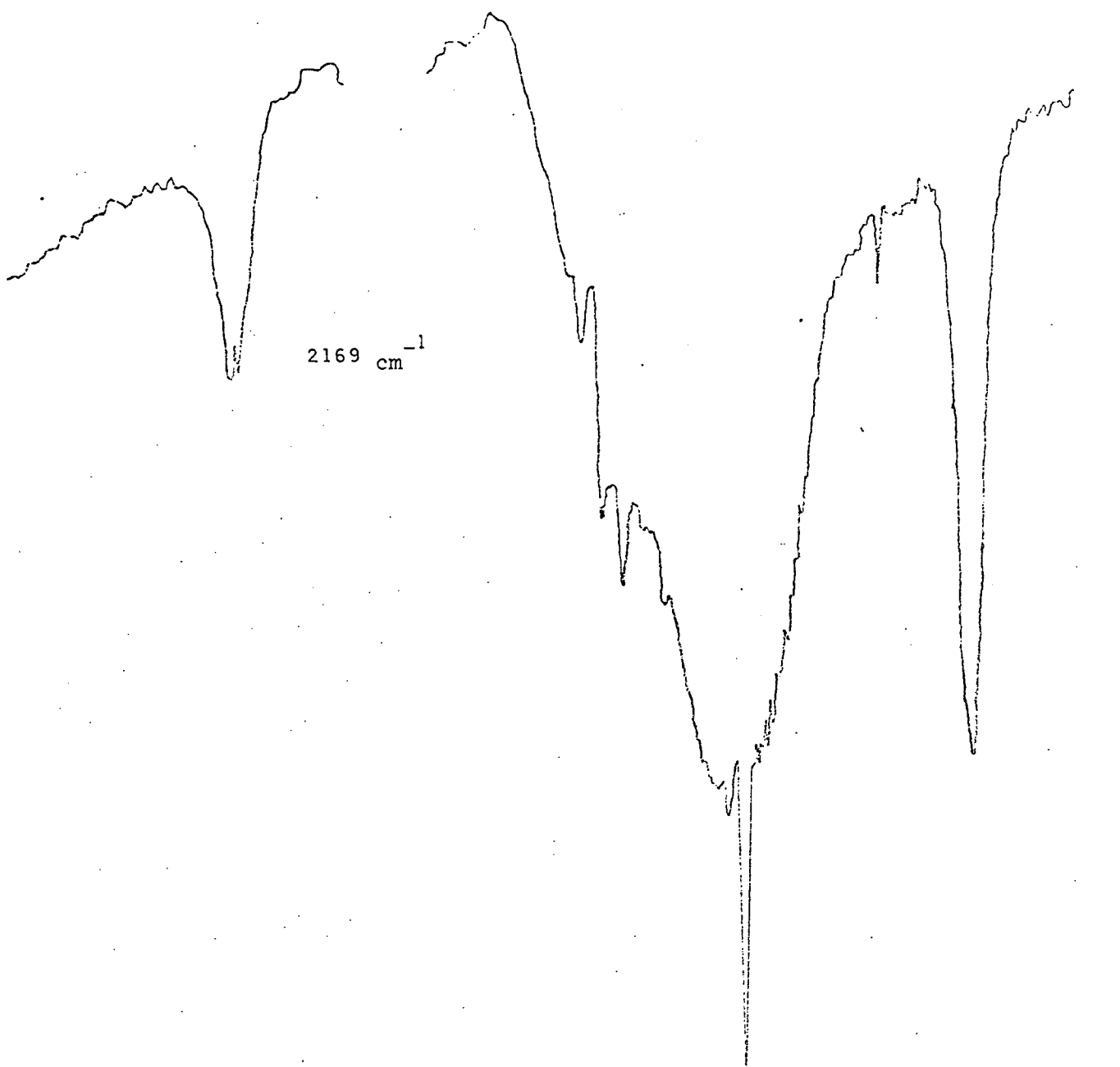
Further evidence for the validity of the method was obtained by conducting a similar experiment over a CeX zeolite catalyst. This catalyst has been shown to give rise to carbonium ion intermediate type reactions⁽⁹²⁾. Infrared spectroscopic analysis of the propylene/ D_2O exchange reaction on the CeX zeolite catalyst indicated strong absorptions for both the 1-propene- $3d_1$ and the 1-propene- $1d_1$ (cis and trans), (see i.r. spectra no. 5), verifying the carbonium ion intermediate promotion characteristics of the catalyst. The above experiment proves that had the tin-antimony-oxide catalysts tended to promote carbonium ion type reactions then the experimental method would have detected the corresponding products.



Infrared Spectra No. 1:- C₃H₆ (6.67 k Nm⁻²).



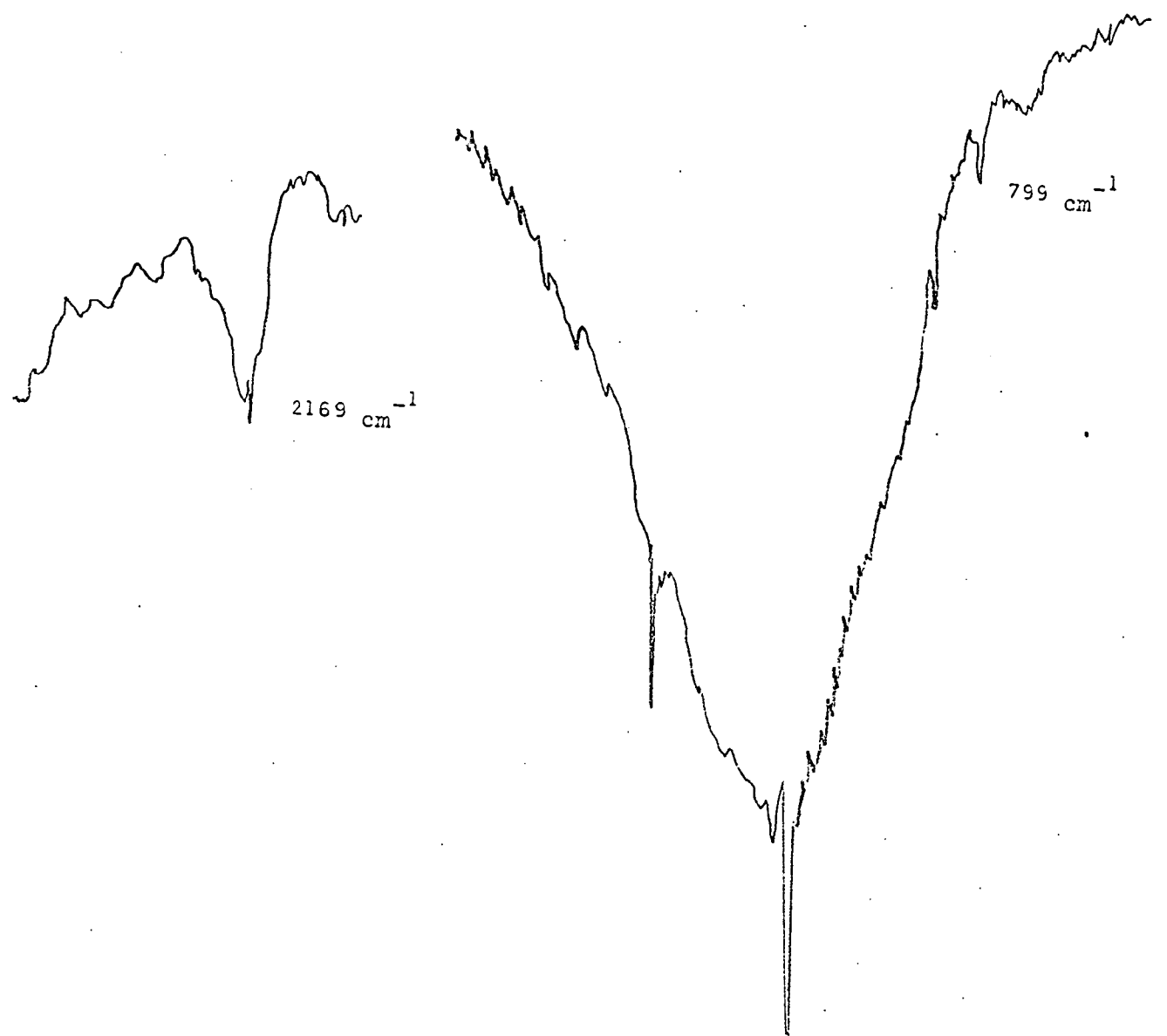
Infrared Spectra No. 2:- CH3-CH=CHD (6.67 k Nm^{-2})



2169 cm^{-1}

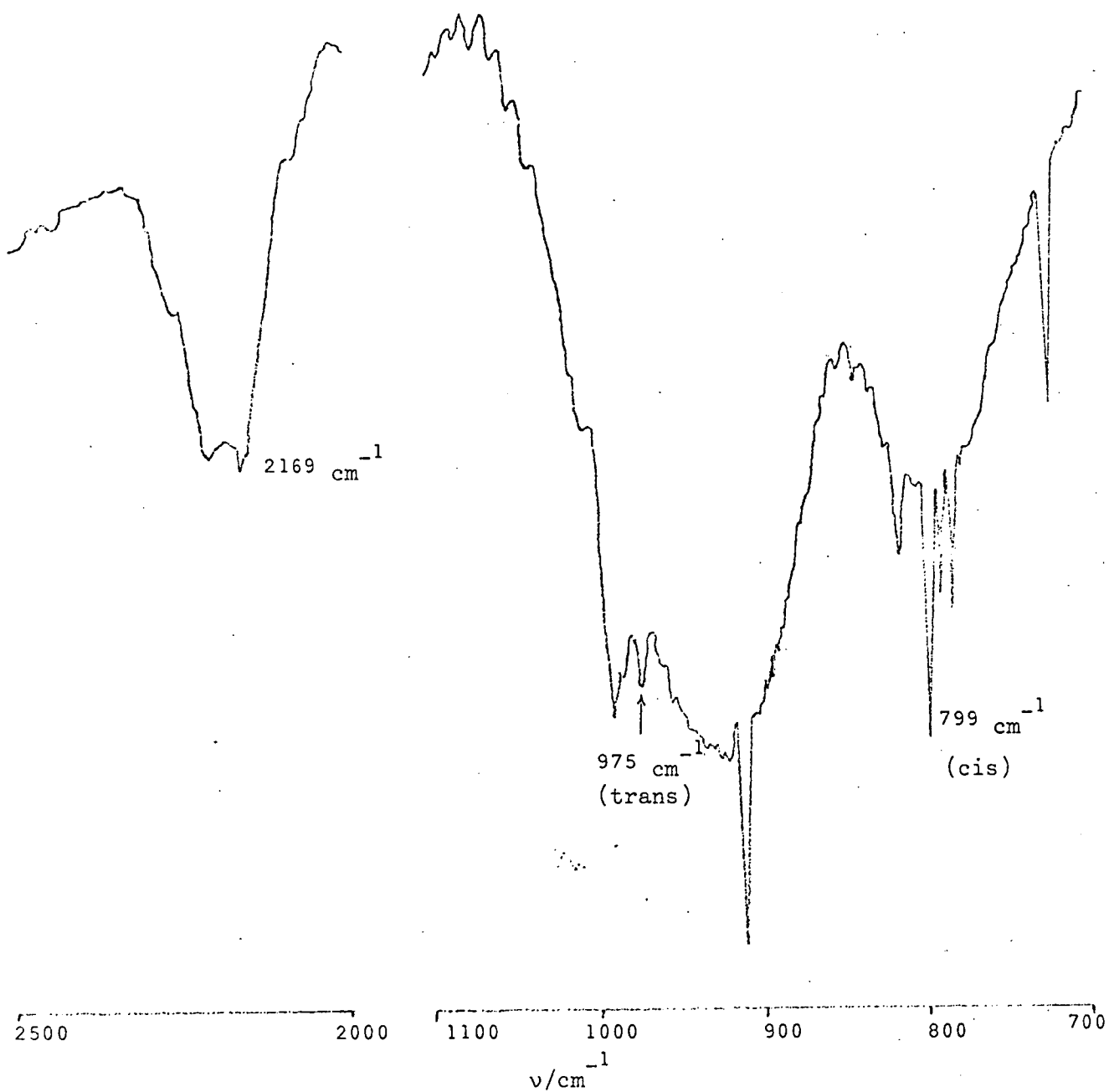
2500 2000 1100 1000 900 800 700
 ν/cm^{-1}

Infrared Spectra No. 3:- $\text{CH}_2\text{D}-\text{CH}=\text{CH}_2$ (6.67 k Nm^{-2})



2500 2000 1100 1000 900 800 700
v/cm⁻¹

Infrared Spectra No. 4:- C₃H₆ + D₂O Reaction Products over tin-antimony-oxide catalyst (6.67 k Nm⁻²).



Infrared Spectra No. 5:- C₃H₆ + D₂O Reaction Products over CeX zeolite catalyst (6.67 k Nm⁻²).

Propylene Oxidation Reactions.

6.1. Introduction.

During the past decade considerable investigation into the propylene oxidation reaction over a number of catalysts, primarily bismuth-molybdenum-oxides, has led to general agreement with regard to the initial stage of the reaction mechanism. The initial step appears to be the abstraction of an allylic hydrogen atom to form a symmetrical allyl intermediate. The subsequent step, abstraction of a second hydrogen atom from either end of the symmetrical intermediate, followed by oxygen atom incorporation to yield acrolein, is less well understood.

The above mechanism provides little or no information with regard to the pathway of oxygen atom incorporation. Isotopic oxygen ($^{18}\text{O}_2$) was, therefore, used in an attempt to determine the mode of oxygen atom incorporation into the oxygen containing products, formed in the catalytic oxidation of propylene over tin-antimony-oxide catalysts.

6.2. Experimental.

The experimental apparatus and catalyst preparation has previously been described in Chapter 4. Reactions were carried out in a silica reaction vessel at temperatures between 523 - 623 K. A reaction mixture consisting of two parts propylene to three parts oxygen -18 was used, in order to prevent severe reduction of the

catalyst. After preparation in the mixing bulb, the reaction mixture was expanded into the reaction vessel to give a pressure of 6.67 k Nm^{-2} (50 mm Hg). Normally, fresh 1 g samples of the catalyst were used in each experiment. The catalyst was activated by outgassing in vacuo for a period of 18 hours at the reaction temperature, prior to admission of the reaction mixture. In some cases pretreatment of the catalyst with $^{18}\text{O}_2$ prior to a run was carried out.

The oxidation reaction was followed by monitoring the peaks with m/e values of 32, 34, 36, 41, 44, 46, 48, 56 and 58 corresponding to $^{16}\text{O}_2$, $^{16}\text{O}^{18}\text{O}$, $^{18}\text{O}_2$, C_3H_6 , C^{16}O_2 , $\text{C}^{16}\text{O}^{18}\text{O}$, C^{18}O_2 , $\text{CH}_2=\text{CH}-\text{CH}^{16}\text{O}$, $\text{CH}_2=\text{CH}-\text{CH}^{18}\text{O}$. Unfortunately the mass spectrometer proved inadequate for quantitative analysis of the water and carbon monoxide species, due to adsorption and oxidation phenomena within the instrument. The M.S.20 mass spectrometer was operated with an electron energy of 70 eV and a response time of 0.1 s. A scan speed of 45, (minutes per complete scan), combined with a rapid response "Telsec 700" heated stylus recorder produced satisfactory mass spectral data for all species. Following the usual corrections for background, natural isotopes and fragmentation, where necessary, the reaction products were plotted in terms of number of moles against reaction time. The number of moles were obtained by reference to previously drawn graphs of the relative sensitivities of the different molecules. The relative sensitivity graphs were constructed by plotting various pressures of pure gases against the appropriate mass spectrometer peak height. Slight day to day fluctuations occurred in the

sensitivity of the mass spectrometer. However, results obtained by this method were fairly consistent and, therefore, may be regarded as providing a good semi-quantitative analysis of the reaction species.

6.3. Results.

Control experiments proved the silica glass reaction vessel to be catalytically inert for propylene oxidation reactions at temperatures up to 623 K. Further control experiments were carried out in order to establish whether or not oxygen exchange occurred in the gas phase between the following pairs of molecules:- $^{16}\text{O}_2$ - $^{18}\text{O}_2$, acrolein (^{16}O) - $^{18}\text{O}_2$, carbon dioxide (^{16}O) - $^{18}\text{O}_2$ and carbon monoxide (^{16}O) - $^{18}\text{O}_2$. Furthermore, acrolein, carbon dioxide, carbon monoxide and oxygen (^{16}O) were exposed to an (^{18}O) pre-exchanged catalyst to ascertain if heterophase exchange occurred between the (^{18}O) atoms of the catalyst and the gas phase species.

The possible exchange reactions were observed by monitoring the appropriate mass spectrometric peaks. In all cases no significant exchange reaction was observed at reaction temperatures up to 623 K, in agreement with Winter's⁽⁸⁷⁾ work which suggested that oxygen exchange over similar catalysts was unlikely to occur at temperatures below 723 K. Therefore, exchange mechanisms were not responsible for the appearance of any (^{18}O) in the propylene oxidation products at the reaction temperatures employed.

Verification that the sensitivity of the mass spectrometer remained constant during the course of a run, was obtained by carrying out a number of oxidation experiments using argon as an internal standard.

The oxidation of a 2:3 mixture of C_3H_6 : $^{18}O_2$ at 573 K was found to occur at a significant rate, over all except the 100 atom % Sb catalyst. A typical example of the gas phase composition for the reaction of C_3H_6 with $^{18}O_2$ at 573 K is shown in Figure 6.1. In agreement with the work of Peacock⁽⁵¹⁾ et al and Keulks⁽⁹³⁾, over bismuth-molybdenum-oxide catalysts, the oxygen was removed from the gas phase faster than the propylene; however, it did not immediately react with the adsorbed propylene. Figure 6.1 indicates that initially, the products contain mainly oxygen -16. However, as the reaction progresses oxygen -18 becomes increasingly incorporated into the oxidation products. For example from Figure 6.1 at 2.5 minutes, 20% of the acrolein produced was acrolein (^{18}O) while at 30 minutes 34% of the acrolein was acrolein (^{18}O). In addition the species $^{16}O_2$ and $^{16}O^{18}O$ were not detected in the gas phase, indicating that the heterophase exchange and homophase equilibration reactions did not occur.

A number of runs were carried out in which the catalyst was pretreated with $^{18}O_2$, (4.00 k Nm⁻² (30 mm Hg) for 18 hours at 723 - 823 K). During this process the $^{16}O_2$ / $^{18}O_2$ exchange reaction was followed by monitoring peaks with m/e values of 32, 34 and 36, the extent of exchange between the gas phase and the catalyst oxygen atoms could then be calculated. On completion of the pretreatment process the gas phase was pumped off for 10 minutes while the temperature was dropped to the 573 K reaction temperature. Then the reaction mixture comprising C_3H_6 : $^{16}O_2$ in the ratio 2:3 was

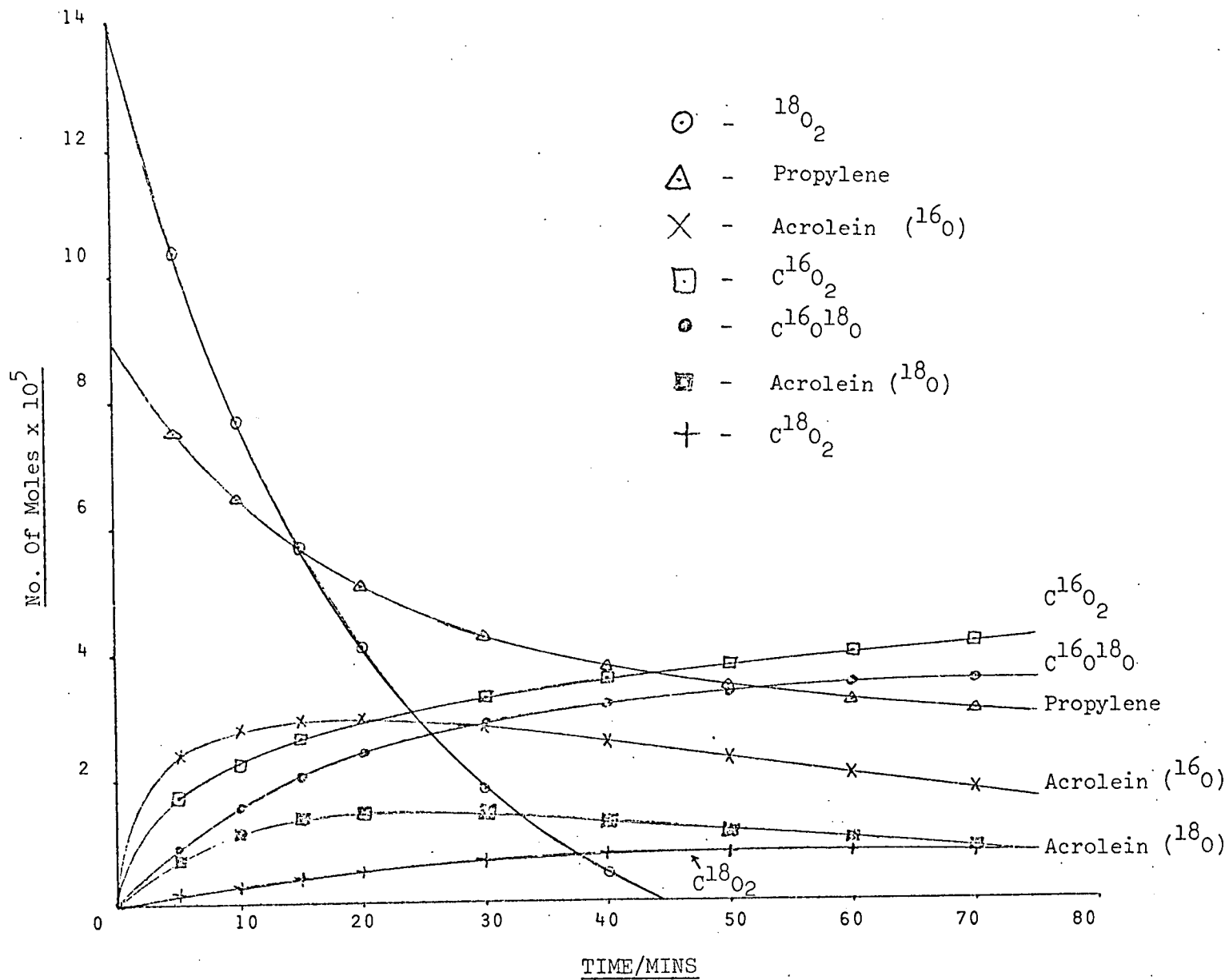


Figure 6.1

$\text{C}_3\text{H}_6/^{18}\text{O}_2$ Reaction On 9.09 Atom % Sb Catalyst At 573 K.

introduced into the reaction vessel and the reaction followed as usual. The only source of ^{18}O was now the ^{18}O which had become incorporated into the catalyst by the pretreatment exchange process. As expected, the products did in fact contain some ^{18}O , the amount varying for different catalysts and % exchange during the pretreatment process.

The results obtained over the 9.09 atom % Sb catalyst will be used to illustrate the method of calculation. However, essentially the same effect, as a consequence of $^{18}\text{O}_2$ pretreatment, was observed over the 6.13, 29.60 and 49.50 atom % Sb catalysts. By monitoring the $^{16}\text{O}_2 / ^{18}\text{O}_2$ exchange reaction the number of oxygen atoms in the catalyst, which undergo exchange and finally end up as ^{18}O atoms, can be calculated. Assuming that 1 m^2 of surface contains 6×10^{18} oxygen atoms, regardless of the crystallographic structure and the exact representation of the surface⁽⁸⁷⁾, then 1 g of the 9.09 atom % Sb catalyst surface contains approximately 12×10^{19} oxygen atoms. At the end of the pretreatment process approximately 2×10^{19} oxygen atoms had been exchanged. Therefore, about one in six of the catalyst oxygen atoms have been changed to ^{18}O (16.7%). The results from the propylene/ $^{16}\text{O}_2$ oxidation run, which was carried out immediately after the pretreatment exchange process, indicated that approximately 14% of the total oxygen atoms in the acrolein and CO_2 oxidation products were (^{18}O). However, a complete assessment of all the oxidation products such as CO and H_2O could not be achieved. These results are in fairly good agreement with the $^{18}\text{O}_2$ pretreatment conclusion that about one in six of the

catalyst oxygen atoms had exchanged.

An extremely rapid initial uptake of propylene from the gas phase by the catalyst was found to occur over all the active catalysts. This phenomenon was detected as a result of a discrepancy between the calculated propylene content of the reaction mixture and the mass spectrometrically determined value at time zero, (extrapolated value). The results indicated that approximately 10% of the calculated propylene content of the reaction mixture had been rapidly adsorbed on to the catalyst surface. This value corresponds to the % propylene adsorbed on to the catalyst surface during the standard propylene pretreatment process, prior to a propylene/D₂O exchange. No such phenomenon was detected for oxygen.

The disappearance of propylene from the gas phase during the initial stages of the reaction was found to obey first order kinetics, as can be seen from Table 6.1 and Figure 6.2. The first order kinetics were plotted according to the equation:-

$$k = \frac{1}{t} 2.303 \log_{10} \frac{C_0}{C}$$

where C₀ and C are the number of moles of propylene in the reaction vessel at time t=0 and time t respectively.

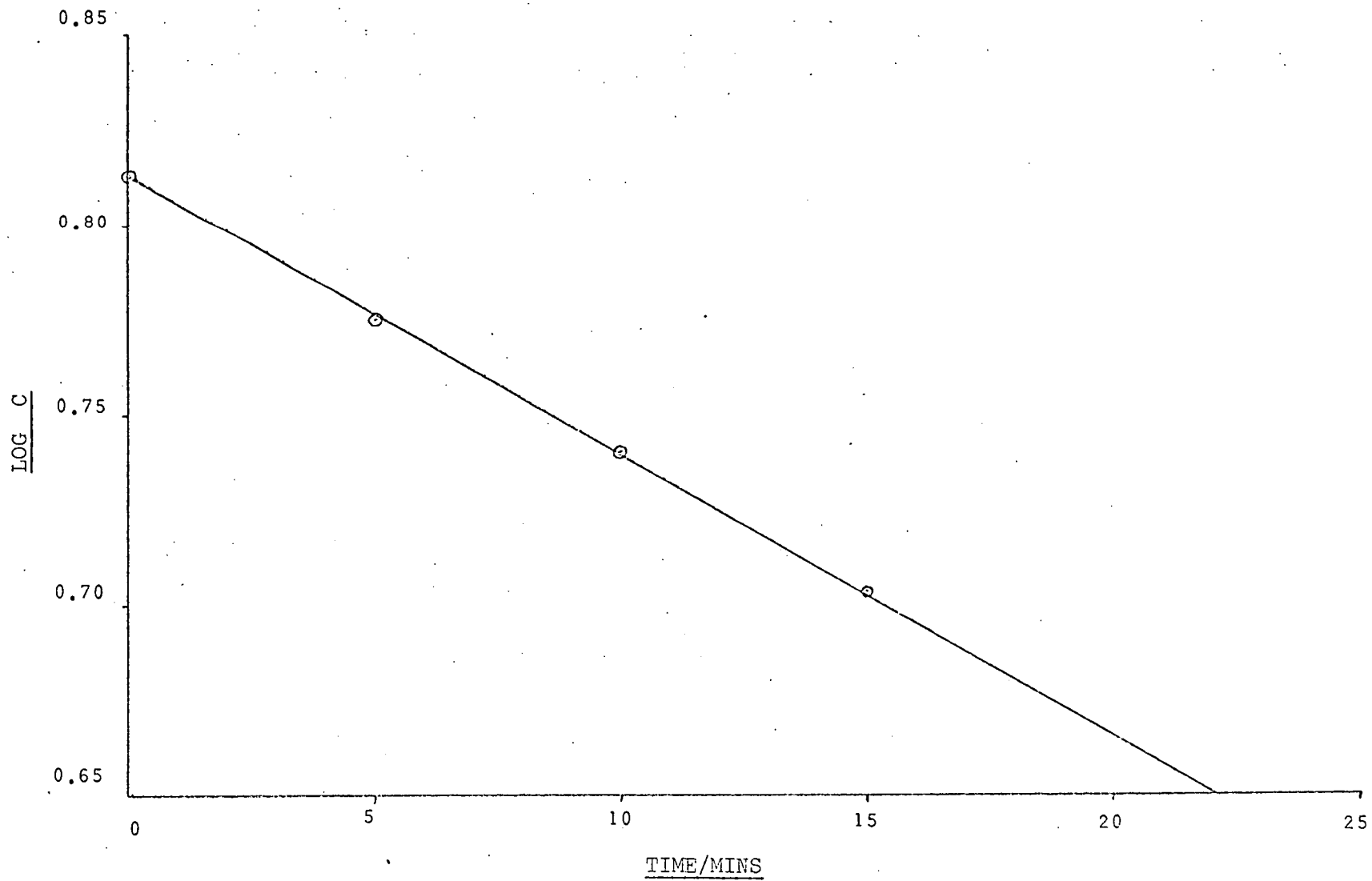


Figure 6.2 First Order Rate Plot For Propylene Disappearance On 29.60 Atom % Sr Catalyst at 573 K.

TABLE 6.1

Propylene oxidation results on 75.00 atom % Sb catalysts at 565 K.

Pressure of Oxygen in the Reaction Vessel (k Nm ⁻²)	Pressure of Propylene in the Reaction Vessel (k Nm ⁻²)	First Order Rate Constant for Propylene disappearance (min ⁻¹)
3.86 (29.0 mm Hg)	1.59 (12.0 mm Hg)	3.21 x 10 ⁻³
3.06 (23.0 mm Hg)	1.65 (12.5 mm Hg)	3.15 x 10 ⁻³
1.57 (11.8 mm Hg)	1.57 (11.8 mm Hg)	3.12 x 10 ⁻³

Application of the following equation, (which implied an oxygen dependence based on the Langmuir adsorption isotherm), to the results, indicated the presence of an oxygen dependence term:-

$$-d[C_3H_6]/dt = k [C_3H_6] [O_2] / (c + [O_2]).$$

where k and c are constants.

The above equation was valid for up to 10% disappearance of oxygen from the gas phase, typical values for k and c are given in Table 6.2.

TABLE 6.2

Typical values for constants k and c after 10% oxygen disappearance during propylene oxidation reactions at 573 K.

Catalyst Composition Atom % Sb	Constant k	Constant c
29.60	0.21 ± 0.002	0.15 ± 0.01
49.50	0.17 ± 0.001	0.11 ± 0.01
75.00	0.10 ± 0.001	0.06 ± 0.01

However, as the percentage disappearance of oxygen from the gas phase increased above 10% then the equation failed, the value of constant c tended to exceed the value of k , typical values were:-

after 30% propylene disappearance $k = 0.39 \pm 0.002$ $c = 1.92 \pm 0.08$

after 60% propylene disappearance $k = 0.62 \pm 0.003$ $c = 4.04 \pm 0.16$

Failure of the equation to be obeyed for the higher percentage oxygen disappearance values, may be due to the rapid removal of oxygen from the gas phase. These results merely serve to indicate the existence of an oxygen dependence term with regard to the overall propylene oxidation reaction.

The results obtained during the initial stages of the reaction were in broad agreement with a first order disappearance for propylene and an

oxygen dependence based on the Langmuir adsorption isotherm. This implied a low concentration of adsorbed propylene and a high concentration of adsorbed, (or surface lattice), oxygen on the catalyst.

Standard runs on fresh 1 g samples of 9.09 atom % Sb were carried out at a number of temperatures, in order to obtain the relevant Arrhenius parameters. An Arrhenius plot was constructed by plotting log first order rate constant for the disappearance of propylene against K/T as shown in Figure 6.3 and from this the activation energy was found to be $33.3 \text{ k J mole}^{-1}$. The Arrhenius parameters obtained from the plot correspond to the equation.

$$r_o = 10^{17.57} e^{-33.3/RT}$$

where r_o is the absolute rate in molecules $\text{sec}^{-1} \text{ m}^{-2}$ and the activation energy is given in k J mole^{-1} . (cf. $r_o = 10^{17.39} e^{-33.2/RT}$ for $\text{C}_3\text{H}_6/\text{D}_2\text{O}$ exchange reaction)

Extrapolation of the Arrhenius plot down to 473 K indicated, that, over the 9.09 atom % Sb catalyst, the rate constant for oxidation was in very good agreement with the rate constant for propylene/ D_2O exchange over a propylene pretreated 9.09 atom % Sb catalyst at 473 K.

Rate constant for oxidation

$$3.45 \times 10^{-3} \text{ min}^{-1}$$

Rate constant for exchange

$$3.25 \times 10^{-3} \text{ min}^{-1}$$

If the specific first order rate constant for the disappearance of propylene from the gas phase is taken as a measure of the rate of oxidation, then a graph of catalytic activity against atom % Sb can be constructed as

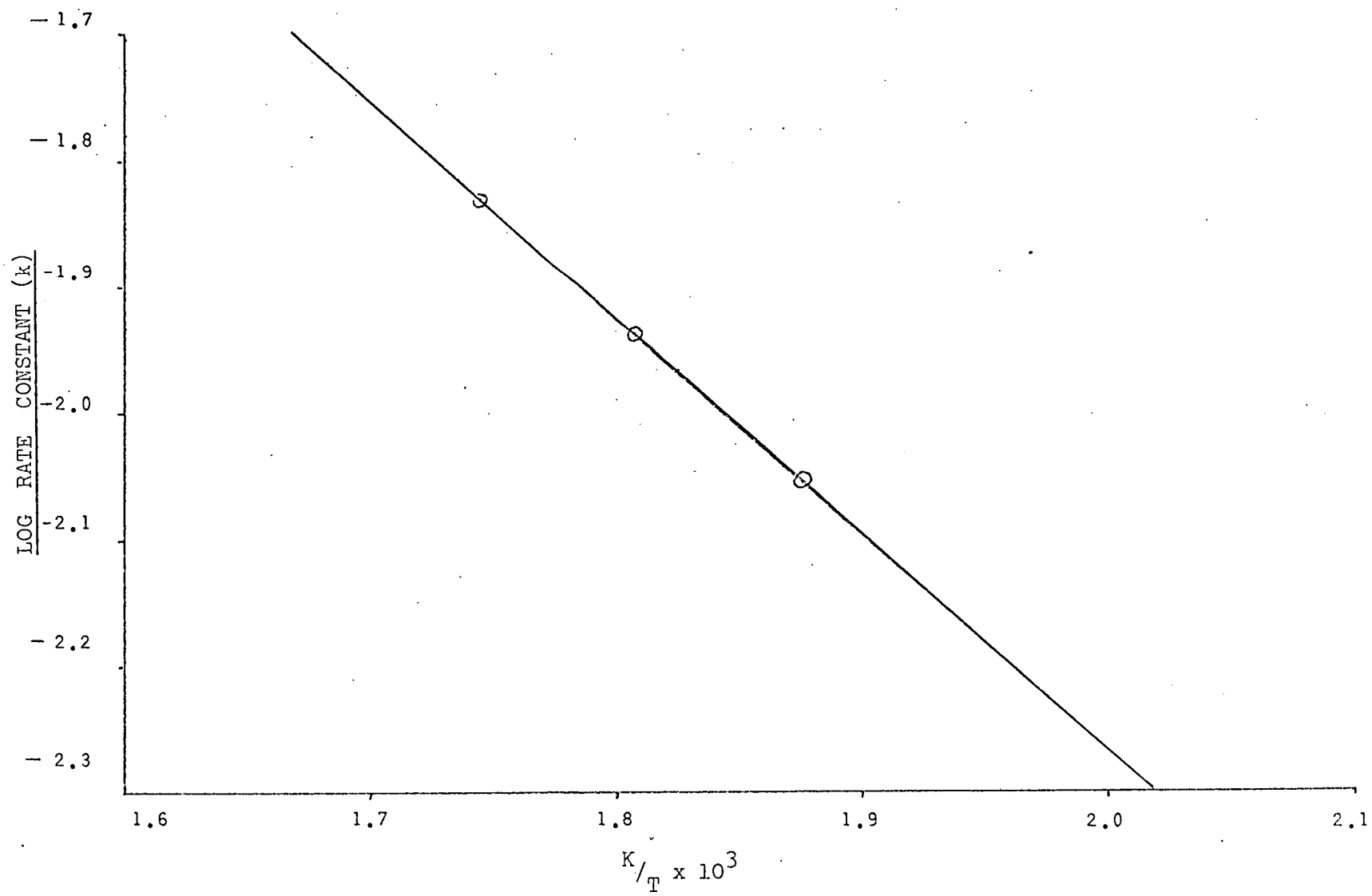


Figure 6.3 Arrhenius Plot For Propylene Oxidation On 9.09 Atom % Sb Catalysts.

in Figure 6.4. The graph displays a measure of the rate of oxidation, at a fixed temperature of 573 K against catalyst composition. A summary of the results for the propylene/ $^{18}\text{O}_2$ oxidation reaction is given in Table 6.3.

Although the rate of oxidation is greatest around 5 atom % Sb the selectivity towards acrolein production is at its lowest, the major products are the carbon oxides. Selectivity, however, increases as the atom % Sb increases though the overall rate of oxidation tends to decrease.

TABLE 6.3
Propylene/ $^{18}\text{O}_2$ Oxidation Reactions.

Catalyst Composition Atom % Sb	Temperature K	First Order Rate Constant For Propylene Disappearance (min^{-1})	Specific First Order Rate Constant For Propylene Disappearance ($\text{min}^{-1} \text{ m}^{-2}$)
Tin Oxide	573	1.68×10^{-3}	0.40×10^{-3}
6.13	573	16.80×10^{-3}	1.38×10^{-3}
9.09	573	13.41×10^{-3}	0.70×10^{-3}
29.60	573	7.08×10^{-3}	0.46×10^{-3}
49.50	573	6.30×10^{-3}	0.50×10^{-3}
75.00	573	4.35×10^{-3}	0.62×10^{-3}
9.09	553	11.62×10^{-3}	
9.09	533	8.84×10^{-3}	

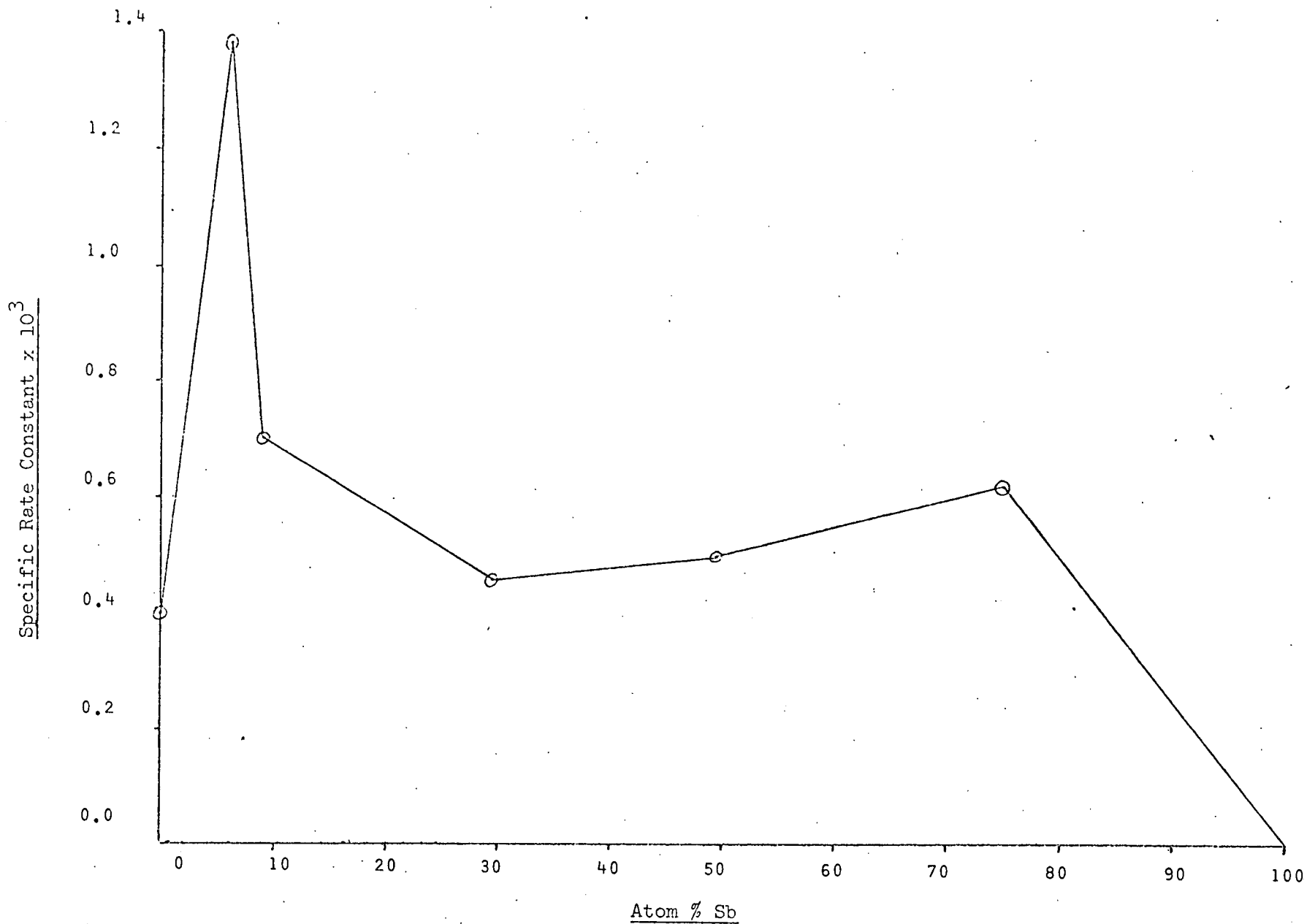


Figure 6.4 Specific Catalytic Activity As A Function Of Catalyst Composition For Propylene Oxidation at 573 K.

6.4. Investigation Of Propylene Oxidation by a Flow System Technique.

6.4.1. Introduction.

The catalytic oxidation of propylene to acrolein over a range of tin-antimony-oxide catalysts has been investigated in a static system. Direct relevance to the full scale plant operation would, however, be greatly enhanced if corresponding results could be obtained by the use of a flow system technique. British Petroleum Chemicals International Ltd., Epsom Division, kindly co-operated to provide the necessary flow system laboratory facilities for just such an investigation.

6.4.2. Experimental.

A flow system was used in which a mixture of propylene, oxygen -16, argon and steam was passed over the catalyst. The reactor containing the catalyst was a 6 mm i.d. silica tube, coiled in the form of a Helix and heated in a thermostatted bath of molten tin. The inlet and effluent gases could be analysed mass spectrometrically by means of two, six port switching valves, located in a heated control box. The effluent gases from the reactor could also be scrubbed countercurrently with water and the products determined by gas chromatographic analysis of the aqueous solution. The inlet gases were analysed for C_3H_6 , acrolein, O_2 , CO_2 , Ar, acrylic acid and aldehydes (by G.L.C.).

Propylene was oxidised over each of the three catalysts, (9.09, 49.50 and 75.00 atom % Sb), under the following conditions:- feed composition $C_3H_6 : O_2 : H_2O : Ar = 5\% : 10\% : 40\% : 45\%$, contact time

= 1, 2 or 4 seconds for each catalyst, temperature range 551 - 703 K. Contact time was defined as (gross volume occupied by the catalyst)/(volume at N.T.P. of gaseous feed per second). After a steady state had been reached it was observed that catalytic activity did not appear to decrease during the course of one run.

6.4.3. Results.

The course of a typical reaction is shown in Figure 6.5 where % yield of products ($\frac{\text{yield}}{C_3H_6 \text{ converted}} \times 100$) is plotted as a function of contact time for a 75.00 atom % Sb catalyst at 678 K. Essentially similar results were obtained for the other two catalysts.

Plots of $\log(a-x)$ Vs contact time were linear, indicating first order behaviour for the disappearance of propylene, as shown in Figure 6.6. Values for k , the first order rate constant, were calculated from the expression:-

$$k = \frac{1}{t} 2.303 \log_{10} \frac{C_0}{C}$$

where t is the contact time in seconds, and C_0 and C are the number of moles of propylene at times zero and t respectively. Arrhenius plots were constructed by plotting $\log k$ Vs $\frac{K}{T}$ as shown in Figure 6.7, and from these the activation energies were calculated as shown in Table 6.4.

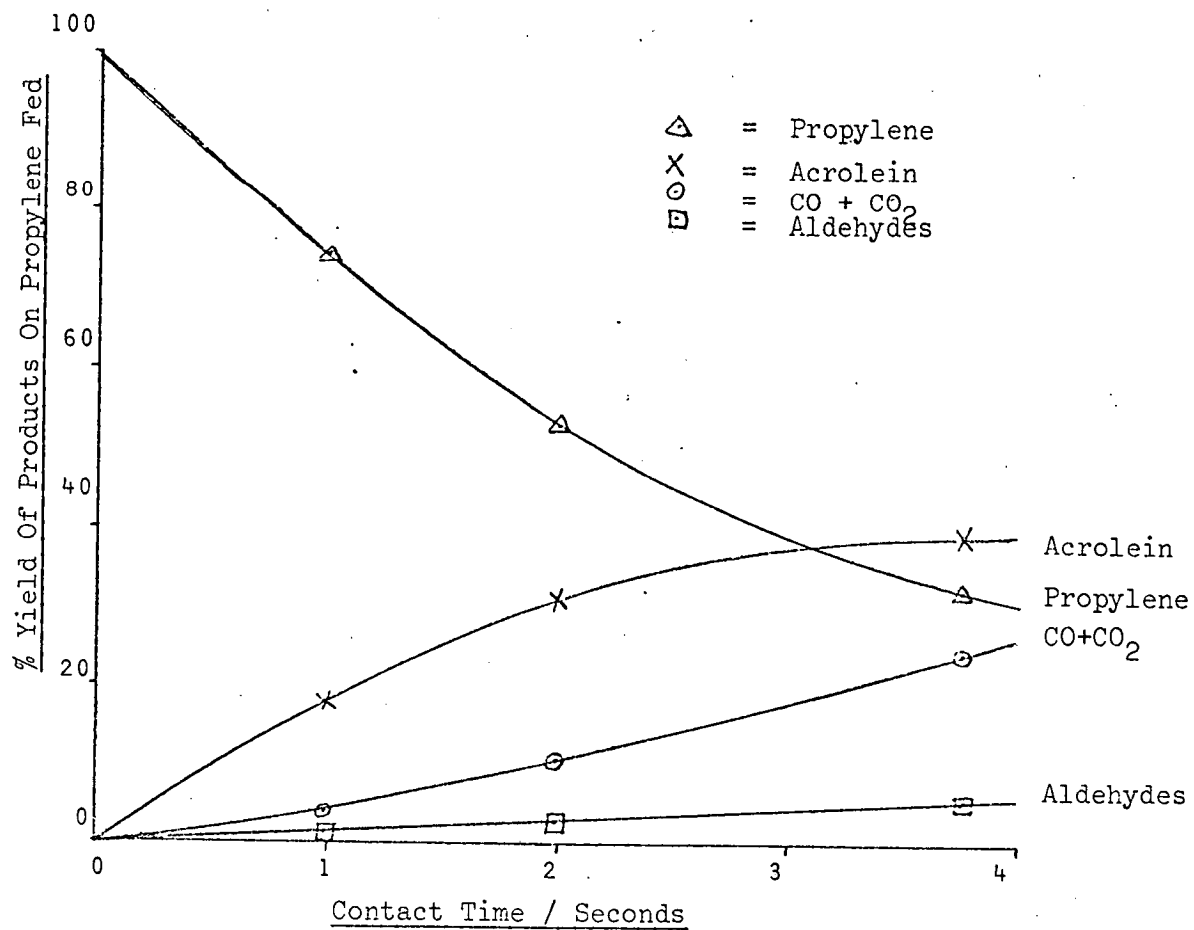


Figure 6.5 Flow System $C_3H_6/^{16}O_2$ Reaction, % Yield Of Products As A Function Of Contact Time For 75.00 Atom % Sb Catalyst At 678 K.

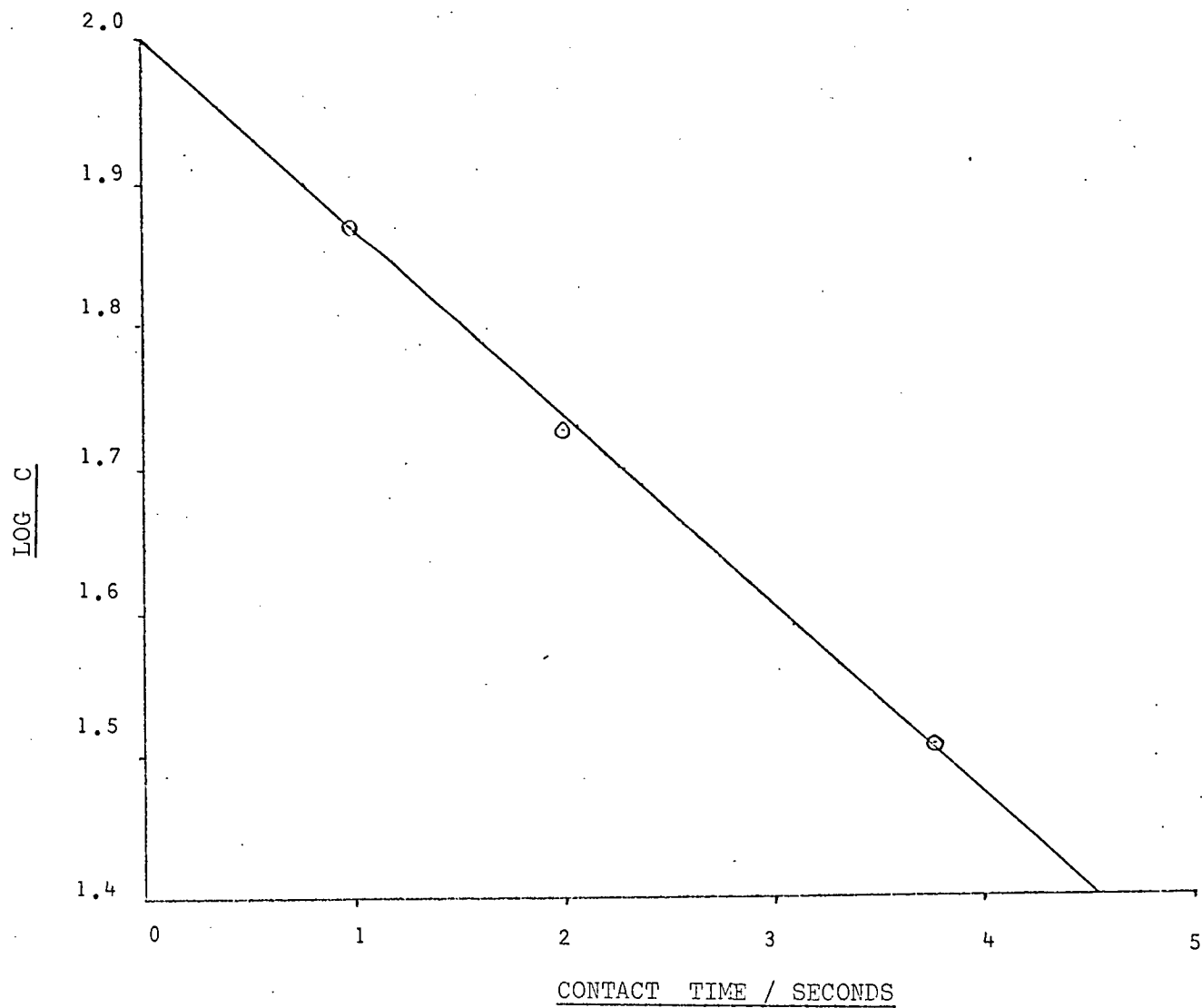


Figure 6.6 Flow System First Order Rate Plot For Propylene Disappearance On 75.00 Atom % Sb Catalyst At 678 K.

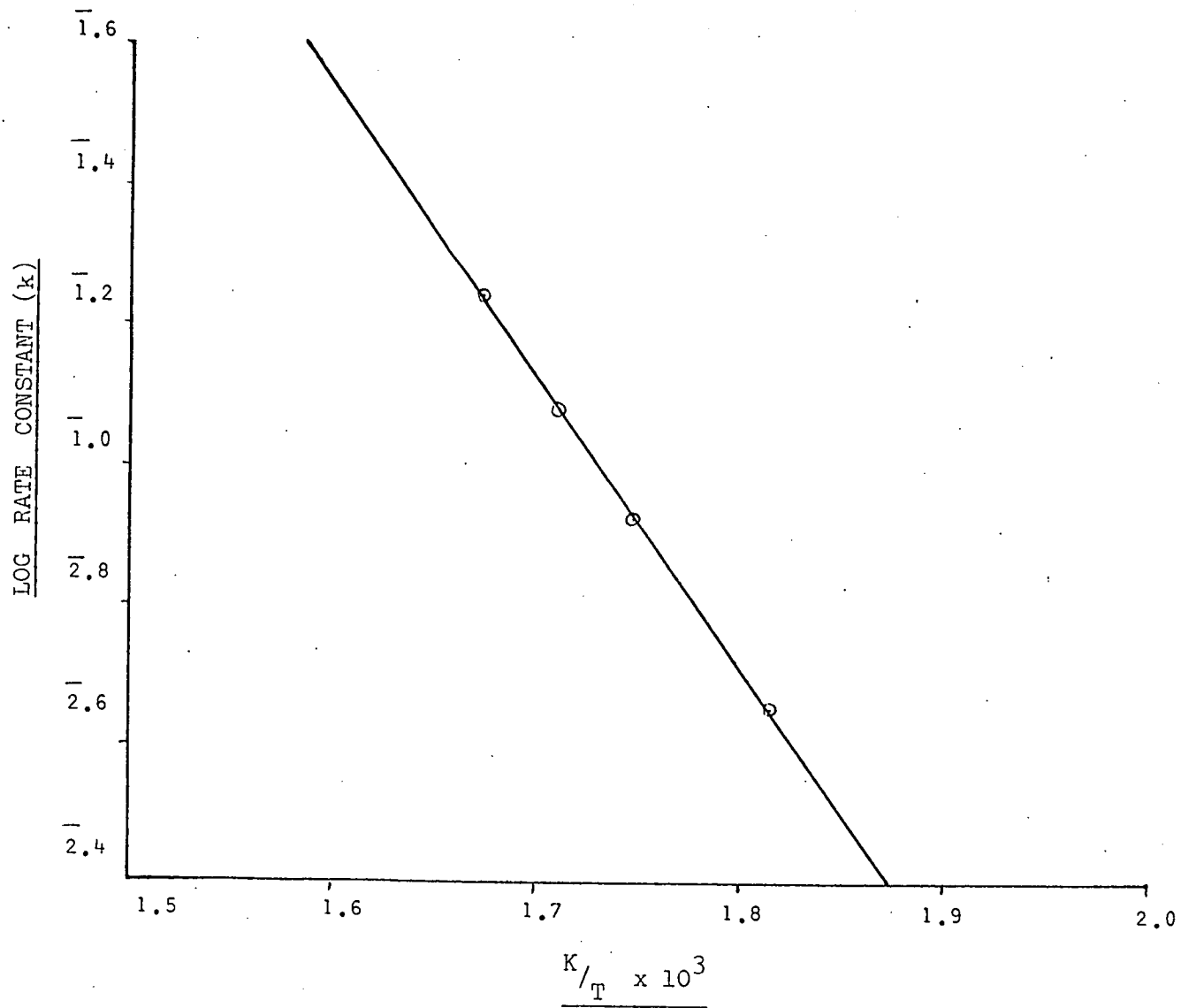


Figure 6.7. Arrhenius Plot For Flow System Propylene Oxidation On 9.09 Atom % Sb Catalysts.

TABLE 6.4.

Energies of Activation for Propylene Oxidation, (Flow System Results).

Catalyst Composition Atom % Sb	Energy of Activation kJ mole ⁻¹
9.09	78.9 ± 5.2
49.50	54.6 ± 10.0
75.00	75.6 ± 6.1

A graph of efficiency of formation of acrolein and CO₂ was obtained by plotting % efficiency, ((% yield of product / % C₃H₆ converted) x 100), against contact time, as shown in Figure 6.8. It may be noted that on extrapolation back to zero time, the plots do not pass through the origin. This indicates that although both acrolein and CO₂ are primary products, CO₂ is also a secondary product.

TABLE 6.5

Comparison between the catalysts with regard to catalytic activity for propylene oxidation, (Flow System Results).

Catalyst Composition Atom % Sb	Contact Time s	Temperature K	% Yield Acrolein	Surface Area _g ⁻¹ m ²
9.09	1.0	585	9.8	19.2
49.50	1.0	678	20.0	12.5
75.00	1.0	678	16.6	7.0

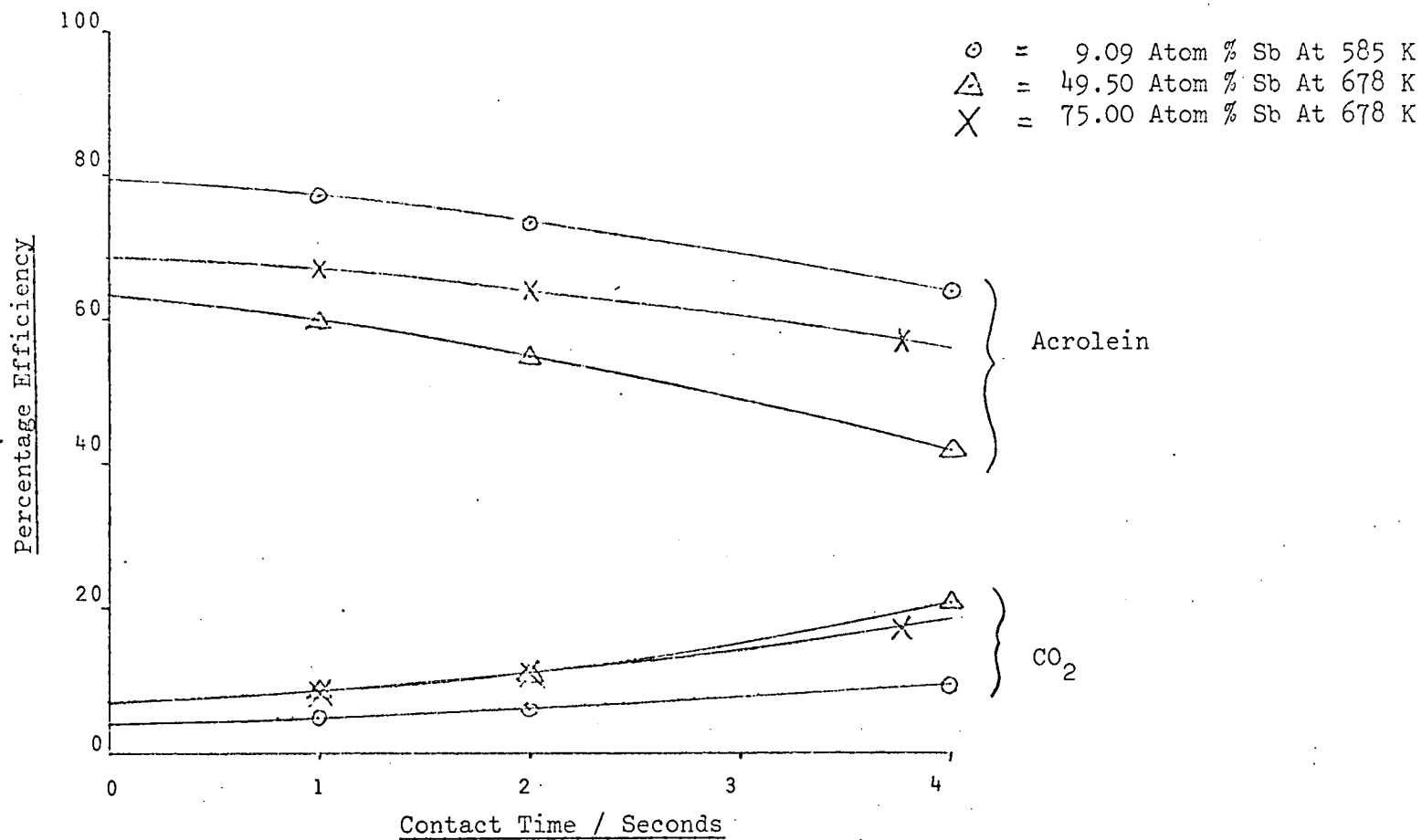


Figure 6.8 Efficiency of Formation of Acrolein And Carbon Dioxide in Flow System Propylene Oxidation.

Table 6.5 indicates the difference in activity between the three catalysts for a one second contact time. At 678 K the 9.09 atom % Sb catalyst was considerably more active than the other two, as all the oxygen was consumed and the catalyst tended to be reduced.

These results, though limited to three catalysts, are in general agreement with the results obtained from the static system and also with the more extensive results published by Godin, McCain and Porter⁽⁵²⁾.

Isotopic Oxygen Exchange between the Gas Phase and
the Solid Catalyst.

7.1. Introduction.

The preceding chapter dealt with the catalytic oxidation of propylene from the oxygen incorporation point of view. However, at the temperatures employed no isotopic $^{16}\text{O}_2$ / $^{18}\text{O}_2$ exchange between the gas phase and the oxide catalyst was observed. Though this exchange process may not be important from the overall oxidation viewpoint an investigation of these reactions was carried out in order to complete the picture and clarify the exchange mechanisms involved.

The initial work in the field of isotopic oxygen exchange between gaseous oxygen and lattice or adsorbed oxygen of solid catalysts, was carried out by Morita and Titani⁽¹¹⁰⁾ around 1940. They produced semiquantitative results on the catalytic exchange of ^{18}O between gaseous oxygen and water vapour over a number of oxide catalysts. Their work was, however, of rather limited scope since the ^{18}O concentration was determined by means of water density measurements. A more sophisticated experimental approach, which employed a static system, with continuous sampling provision for mass spectral analysis, was introduced by Winter⁽⁹⁴⁾ in 1949.

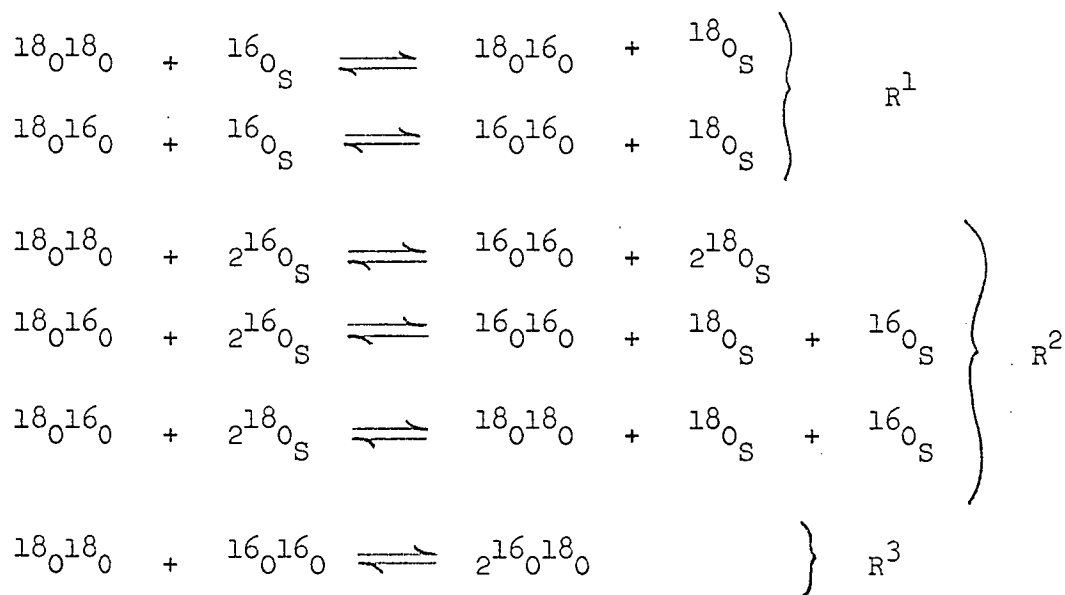
Since 1950, many workers have joined the field, the most notable being Margolis, Boreskov, Jiru and Novakova from the Russian and Czechoslovakian schools. Consequently a large amount of experimental

data, relevant to heterophase exchange, homophase equilibration and lattice oxygen diffusion, has been published. A comprehensive kinetic treatment has been put forward by Klier, Novakova and Jiru⁽⁹⁵⁾ and has been verified by Winter⁽⁸⁷⁾, who then attempted to classify various oxides according to their respective oxygen exchange mechanisms.

The subject has been extensively discussed and reviewed by those most active in the field, namely Winter⁽⁹⁶⁾, Boreskov⁽⁹⁷⁾ and Novakova⁽⁹⁸⁾.

7.2. Kinetics.

The exchange reactions of ^{18}O and ^{16}O which can occur in a system containing gaseous oxygen and a solid oxide are described by the following equations:-

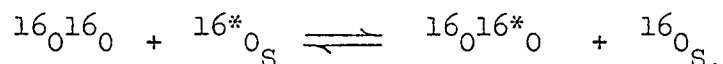


where R^1 denotes the number of elementary acts of exchange per unit time, in which one molecule exchanges one oxygen atom with the oxide.

R^2 , the number of acts per unit time in which one molecule exchanges two atoms with the oxide.

R^3 , the number of molecules per unit time exchanging their atom with another oxygen molecule.

The scheme does not include reactions in which exchange occurs but does not lead to a change in isotopic composition e.g.



Before the kinetics can be discussed further a number of important assumptions must be made.

- (1) That the ^{constants} rates of the forward and reverse reactions are equal.
- (2) That the reactions are taking place in a closed system containing a fixed quantity of gaseous oxygen and of oxide, the samples withdrawn for analysis being very small.
- (3) The experimental conditions are such that one or more of the above reactions is/are rate determining, so that diffusion of oxygen in the gas or solid phase does not effect the kinetics.
- (4) That the number of exchangeable oxygen atoms in the surface is well defined.
- (5) That all the exchangeable oxide atoms are equivalent.

The kinetics of the exchange involving the above three reactions have been extensively discussed, and relevant kinetic expressions deduced by Boreskov⁽⁹⁷⁾ and by Klier, Novakova and Jiru⁽⁹⁵⁾. The kinetic expressions derivable from the above equations now follow, but for a rigorous treatment the above paper by Klier, Novakova and Jiru must be consulted.

The following symbols are employed throughout:-

x = number of molecules of $^{18}\text{O}_2$ in the gas phase.

y = number of molecules of $^{16}\text{O}^{18}\text{O}$ in the gas phase.

z = number of molecules of $^{16}\text{O}_2$ in the gas phase.

u = number of exchangeable ^{18}O atoms in the solid oxide.

v = number of exchangeable ^{16}O atoms in the solid oxide.

$$x+y+z = a$$

$$2x+y = w$$

$$v+u = m$$

$$w+u = c$$

So that in a gas in statistical equilibrium

$$K_{\text{equil}} = \frac{y^2}{xz} = 4.$$

In general it can be shown that

$$-\frac{dw}{dt} = (2R^2+R^1) \left(\frac{2a+m}{2am} \right) (w-w_{\infty}) \quad \text{---7.1}$$

or

$$\frac{w-w_{\infty}}{w_0-w_{\infty}} = \exp - \left\{ (2R^2+R^1) \left(\frac{2a+m}{2am} \right) \right\} t \quad \text{---7.2}$$

where w_0 is the initial value of w and w_{∞} is the value at $t = \infty$, w being the total number of ^{18}O atoms in the gas phase.

Considering the initial reactions R^1 , R^2 and R^3 we find that

$$-\frac{dx}{dt} = R^1 \left(\frac{xv}{am} - \frac{yu}{2am} \right) + R^2 \left(\frac{xv^2}{am^2} - \frac{zu^2}{am^2} + \frac{2xuv}{am^2} - \frac{yu^2}{am^2} \right) + \frac{R^3}{2} \left(\frac{2xz}{a^2} - \frac{y^2}{2a^2} \right)$$

Since $\frac{dw}{dt} = \frac{2dx}{dt} + \frac{dy}{dt}$

then as $-\frac{dw}{dt} = (2R^2 + R^1) \left(\frac{2a+m}{2am} \right) (w-w_\infty)$

the solution for x is

$$x = A + B \exp(-Xt) + C \exp(-2Xt) + (x_0 - A - B - C) \exp(-Yt)$$

where

$$A = \frac{ac^2}{(2a+m)^2}$$

$$B = \frac{(w_0 - w_\infty)(c)}{(2a+m)}$$

$$C = \frac{(w_0 - w_\infty)^2}{2m} \frac{\left[1 + \frac{m^2 R^3}{4aR^2} - \frac{mR^1}{2aR^2} \right]}{\left[2 + \left(\frac{m}{2a} \right) - \left(\frac{mR^3}{2aR^2} \right) + \left(\frac{R^1}{R^2} \right) \right]}$$

$$X = (2R^2 + R^1) \frac{(2a+m)}{2am}$$

$$Y = \frac{R^1 + R^2 + R^3}{a}$$

Theoretically all three rate constants R^1 , R^2 and R^3 may be obtained from one experiment, in which the time dependences of x and y are followed. This requires a complex mathematical approach which involves obtaining best fit theoretical dependences and comparing these dependences with experimentally obtained values and is best carried out by computer.

In view of the complexity of the above approach a more simplified approach may prove satisfactory. When $R^3 \approx 0$ and $R^1 \approx R^2$ then by choosing the experimental conditions such that $m \gg 2a$ and using an initially high concentration of mass 36 in the gas phase, so that $y < x$, it is found that a plot of $\log(x)$ Vs time is initially a straight line of slope closely approximating to

$$\frac{R^1 + R^2 + R^3}{a}$$

A plot of $\log(w - w_\infty)$ against time, from the same run gives $(2R^2 + R^1) \frac{(2a+m)}{2am}$

Thus, from these two plots we may evaluate R^1 and R^2 .

It must be stressed that in cases where R^1 is of the same order as R^2 , the complexities of the equations involved coupled with the experimental errors in measuring x , y and z mean that R^1 and R^2 are each known to only $\pm 20\%$. However, greater reliability can be placed on the value of $(2R^2 + R^1)$ obtained from equation 7.2.

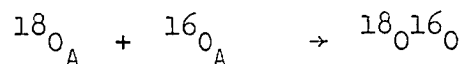
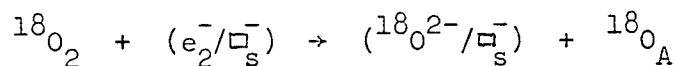
As it is a first order equation a plot of $\log \frac{w - w_\infty}{w_0 - w_\infty}$ against time will give a straight line of gradient $-(2R^2 + R^1) \left(\frac{2a+m}{2am} \right)$.

a and m can be calculated from the quantities used and thus, a value for $2R^2 + R^1$ can be obtained.

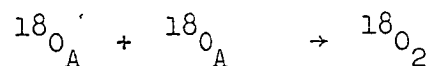
7.3. Mechanisms.

In his review article Winter⁽⁹⁶⁾ concluded that exchange reactions were limited by the adsorption/desorption of oxygen, one of these two processes being the rate determining step. It has since been shown, both by Boreskov et al⁽⁹⁹⁾ and Winter⁽⁸⁷⁾, that the desorption step is in fact the rate determining step for a large number of oxides studied. Winter⁽⁸⁷⁾ has concluded that reactions of rate R^1 are all based on the desorption step.

Thus, for reactions of rate R^1 , the exchange may take place effectively as written or the oxygen molecule may dissociate on adsorption, one atom being immediately incorporated in the surface and the other migrating over the surface until it meets another adsorbed atom when it desorbs as a molecule of oxygen:-

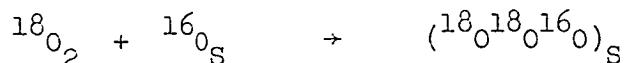


or



where \square_s^- represents an anion vacancy.

The formation of a transient three - atom complex of oxygen on adsorption of a molecule at an exchange site, may also be postulated.



this complex can then decompose to give $\text{O}_2 + \text{O}_S$ in three ways, two giving gaseous $^{18}\text{O}^{16}\text{O}$ and one $^{18}\text{O}_2$.

For reactions of rate R^2 the exchange may occur by the adsorption and simultaneous incorporation into the surface layer of an oxygen molecule from the gas phase, two neighbouring oxygen ions being at the same time desorbed as a gaseous molecule. It is also possible that the exchange may occur by the formation and subsequent decomposition of a transient four atom complex:-

$(^{18}\text{O}^{18}\text{O}^{16}\text{O}^{16}\text{O})_s$ decomposition giving
either $^{18}\text{O}_2$, $^{16}\text{O}_2$ or $^{16}\text{O}^{18}\text{O}$ in the gas phase.

Reactions of rate R^3 , that of equilibration or homomolecular exchange, are catalysed by the surface and lead under normal experimental conditions to no detectable exchange between gas and surface. The mechanism of this reaction is not yet clear, but it may involve adsorbed oxygen in a highly active state or non-stoichiometric metal ions⁽¹⁰⁰⁾.

7.4. Experimental.

The experimental apparatus and catalyst preparation has been described previously in Chapter 4. Reactions were carried out in a silica glass reaction vessel at temperatures between 703 - 873 K. A reaction mixture comprising 50% $^{18}\text{O}_2$ and 50% $^{16}\text{O}_2$ was used in most cases, expansion into the reaction vessel giving a pressure of 2.93 k Nm^{-2} (22 mm Hg). Fresh 4 g samples of the catalyst were used in each experiment. The catalyst was activated by outgassing in vacuo for 18 or 24 hours at the reaction temperature, prior to admission of the reaction mixture. In a number of cases pretreatment of the catalyst with $^{16}\text{O}_2$, after outgassing and prior to reaction, was carried out.

The isotopic exchange reaction was followed by monitoring the peaks with m/e values of 32, 34 and 36 corresponding to the $^{16}\text{O}_2$, $^{16}\text{O}^{18}\text{O}$ and $^{18}\text{O}_2$ species respectively. The M.S.20 mass spectrometer was operated under the same conditions as detailed in Chapter 6.2. Following the necessary corrections, the mass spectral data was converted into percentage of isotopic species.

A graph of $\log \frac{w-w_\infty}{w_0-w_\infty}$ Vs time produced a linear plot of gradient $-(2R^2+R^1) \left(\frac{2a+m}{2am} \right)$.

The values of a and m were calculated from the initial quantities of reactants while the w_∞ value was obtained from a plot of w Vs time. The values of $2R^2+R^1$ obtained over different catalysts were then corrected for surface area and used to give a direct measure of the rate of reaction. The corresponding values of R^1+R^2 were obtained from the linear plot of $\log(x)$ against time, as discussed in section 7.2. * Footnote.

7.5. Results.

Control experiments proved the silica glass reaction vessel to be catalytically inert for isotopic oxygen exchange reactions between the gas phase and the catalyst. The isotopic oxygen exchange reaction was found to occur, at a significant rate, over the more active catalysts at temperatures around 773 K. Linear first order plots were obtained for the graph of

* Footnote:- The author wishes to thank Miss L. Walker and Mr. W.N.B. Greig for their assistance with the experimental work.

$\log \frac{w-w_{\infty}}{w_0-w_{\infty}}$ against time and from the gradient the appropriate values of $2R^2+R^1$ could be calculated; a typical graph is shown in Figure 7.1. In a number of cases the plot of $\log \frac{w-w_{\infty}}{w_0-w_{\infty}}$ against time tended to deviate from linearity, the curvature commencing at about the point where the $K_{\text{equilibrium}}$ value was obtained.

The isotopic exchange reaction was found to be fairly rapid for the Sn oxide and 6.13 atom % Sb catalysts at 773 K. However, as the atom % Sb was increased so the rate of the exchange reaction, as measured by comparison of the respective $2R^2+R^1$ values decreased substantially, so much so, that the reaction temperature had to be increased in order to promote an observable rate of exchange. Reactions were not carried out on either the 75.00 or 100.00 atom % Sb catalysts as preliminary experiments indicated that the rate of exchange at 873 K was extremely slow. Table 7.1 summarises the results obtained over the various catalysts.

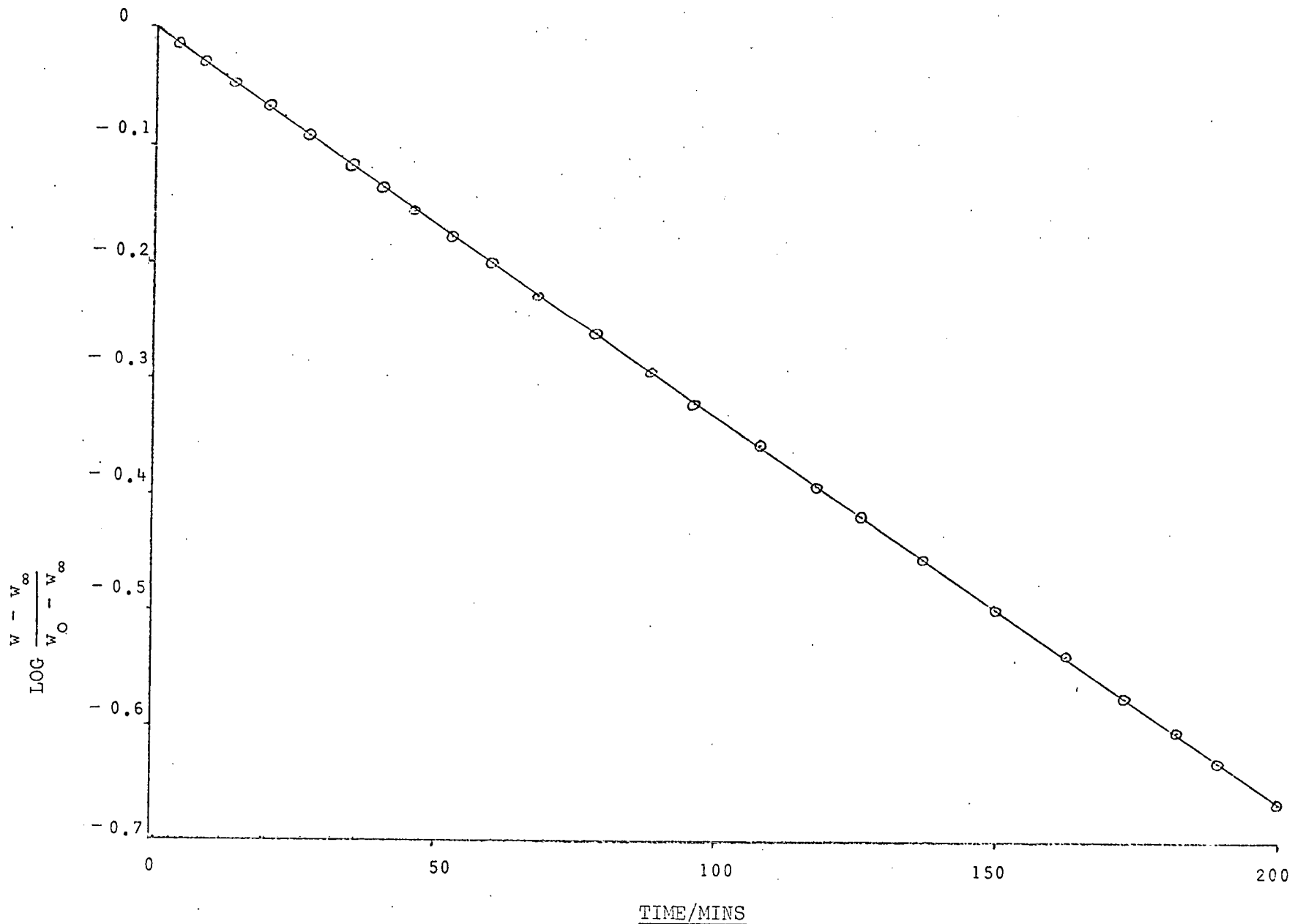


Figure 7.1 First Order Rate Plot For Isotopic Oxygen Exchange On 29.60 Atom % Sb Catalyst At 813 K.

TABLE 7.1

Isotopic Oxygen Exchange Reactions.

Catalyst Composition Atom % Sb	Temperature K	Rate Constant $2R^2+R^1$ (mols min ⁻¹ m ⁻²)	Rate Constant R^2+R^1 (mols min ⁻¹ m ⁻²)
Tin Oxide	773	1.77×10^{13}	1.74×10^{13}
Tin Oxide	713	5.51×10^{12}	
6.13	773	2.01×10^{13}	1.90×10^{13}
9.09	773	1.77×10^{12}	1.05×10^{12}
9.09 treated with $^{16}O_2$	773	1.70×10^{12}	
29.60	813	7.26×10^{11}	
49.50	853	2.32×10^{11}	
Tin Oxide	748	7.82×10^{12}	7.80×10^{12}
6.13	748	6.25×10^{12}	6.23×10^{12}
9.09	748	4.44×10^{11}	3.14×10^{11}

Catalyst surface reproducibility was thought to be critical, therefore, fresh samples of catalyst were used for each experiment. The catalyst activation procedure of outgassing in vacuo at the reaction temperature for 18 or 24 hours prior to admission of the reaction mixture was found to yield reproducible experimental results. In a few cases the catalysts

were pretreated with 4.00 k Nm^{-2} (30 mm Hg) $^{16}\text{O}_2$ for 18 hours at the reaction temperature, after outgassing and prior to reaction. The gas phase was then pumped off for 5 minutes prior to admission of the reaction mixture. In each case the experimental results obtained were not significantly different from those obtained over a standard outgassed catalyst under similar experimental conditions, indicating that catalyst surface reproducibility was satisfactory.

The R^1+R^2 rate constant was calculated for the tin oxide, 6.13 and 9.09 atom % Sb catalysts. The required $\log(x)$ Vs time plot was, however, unsatisfactory for catalysts with higher atom % Sb content. The corresponding values of the $2R^2+R^1$ and the R^1+R^2 rate constants are given in Table 7.1.

An Arrhenius plot was constructed by plotting \log of the $2R^2+R^1$ rate constant against K/T for the 6.13 atom % Sb catalyst. From the plot shown in Figure 7.2, based on data given in Table 7.2, the activation energy was calculated to be $148.0 \text{ k J mole}^{-1}$.

TABLE 7.2

Arrhenius Data for Isotopic Oxygen Exchange.

Catalyst Composition Atom % Sb	Temperature K	$K/T \times 10^3$	$k \times 10^{-12}$	$-12+\log k$
6.13	746	1.340	5.25	0.720
6.13	724	1.380	2.52	0.401
6.13	704	1.420	1.20	0.079

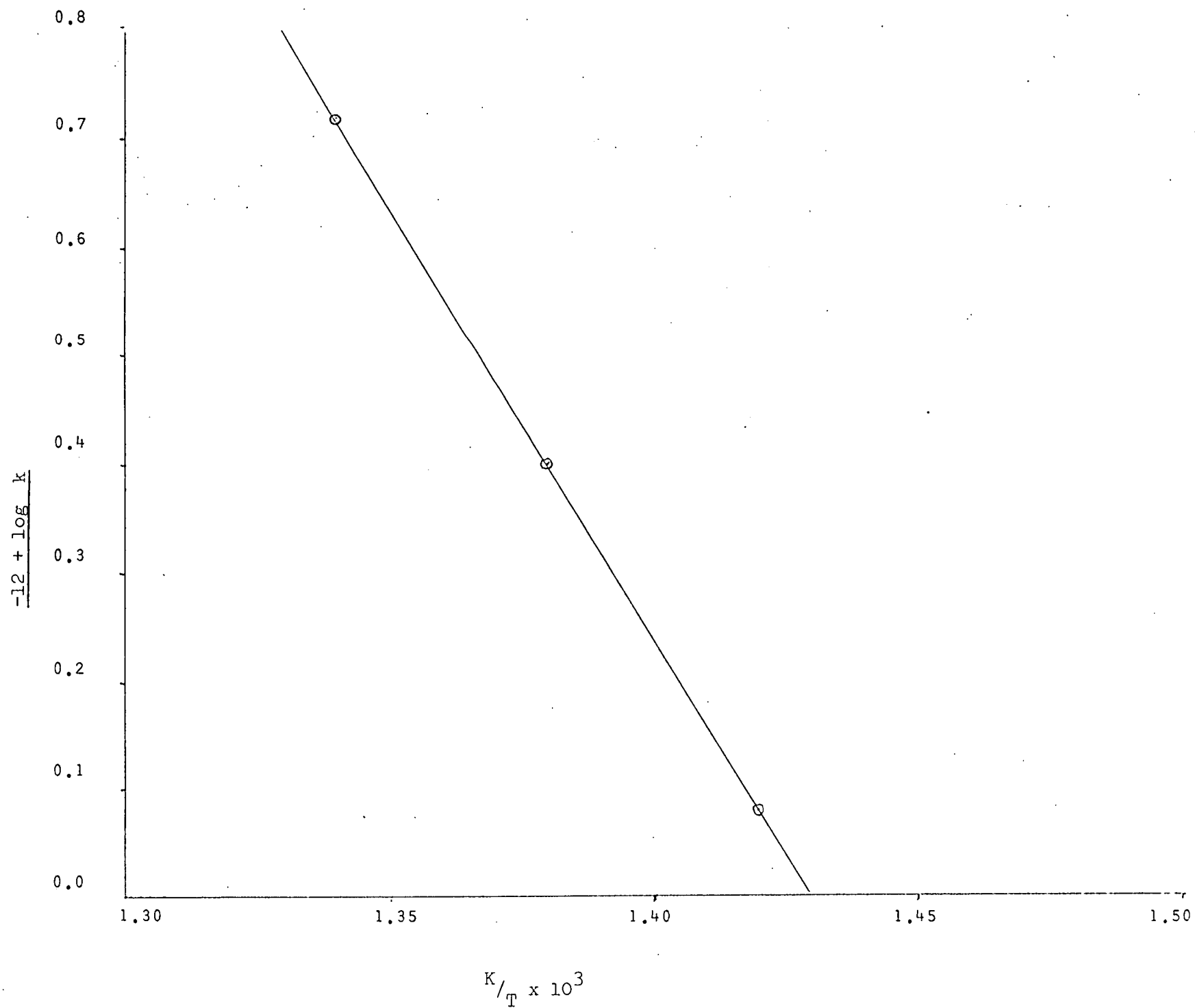


Figure 7.2. Arrhenius Plot for Isotopic Oxygen Exchange On 6.13 Atom % Sb Catalysts.

PART III

DISCUSSION AND CONCLUSION

CHAPTER 8.Discussion

The propylene/D₂O exchange reaction was found to occur over all but the 100 atom % Sb catalyst. In every case the rate of the exchange reaction, over non-treated catalysts, was found to decrease with time, the effect being more pronounced for the most active catalysts. This decrease in rate was accompanied by a marked loss of propylene from the gas phase. These observations indicate clearly that catalysts which had only been outgassed, prior to admission of the reaction mixture, possess highly active sites which can be progressively poisoned by propylene. The typical curved first order rate plot shown in Figure 5.1, indicated that the rate ^{constant} of the exchange reaction was decreasing with time, possibly due to poisoning of the active sites on the catalyst. Curvature was, however, not pronounced until approximately 60% of the reaction was completed. The simultaneous loss of propylene from the gas phase leads one to suspect that the poisoning effect is evidently associated with a strong adsorption of propylene on to the catalyst surface or with polymerisation and/or oxidation of the olefin on the catalyst surface. However, at the temperatures employed very little of the polymer or oxidation products were desorbed from the catalyst surface. The initial formation of a small quantity of acrolein, could indicate that propylene had been oxidised to acrolein by a number of highly active sites which rapidly became exhausted.

Evidence to support the propylene poisoning theory, resulting in loss of catalytic activity, was obtained by conducting carbon analysis on used catalysts. The results produced very good agreement between the total loss of carbon from the gas phase and the quantity of carbon residues found on the catalyst surface. Further evidence arose from the fact that regeneration of the catalyst could be effected by heating in air at 673 K, which would cause the carbon residues to be burned off.

Pretreatment of the outgassed catalyst with propylene resulted in steady catalytic activity and linear first order rate behaviour as shown in Figure 5.2. The effect of propylene pretreatment was probably due to partial poisoning of the more highly active sites on the catalyst surface, by the strong adsorption of propylene. Support for this theory was obtained by the observations that, no acrolein was detected over propylene pretreated catalysts, and that loss of propylene from the gas phase was considerably reduced over these same catalysts. Once again good agreement was obtained between the loss of carbon from the gas phase and the amount of carbon residues found on the pretreated catalyst surface.

Pretreatment of the outgassed catalyst with D_2O , resulted in an increase in the initial rate of exchange for a considerable period of the reaction. Eventually propylene poisoning or exhaustion of the active sites produced curvature of the first order plot, as shown in Figure 5.6. Heavy water pretreatment experiments indicated that replacement of a number of labile hydroxyl groups by deuterioxyl groups on the catalyst surface, seemed highly likely⁽⁸⁶⁾. Evidence to support this claim resulted from

the considerable amount of exchange undergone by propylene, when admitted as the only reactant to a heavy water pretreated catalyst. The results of the heavy water pretreatment indicate that over the 6.13 and 9.09 atom % Sb catalysts:-

(1) Approximately 30-60% of the possible -OD sites are active for exchange. The number of active sites appear to be decreased by doubling the antimony content.

(2) 80-85% of the propylene molecules were involved in the exchange reactions, (total number of propylene molecules = 1.6×10^{19}).

Observation (1) suggests that:-

(a) 30-60% of all possible sites have exchanged with the D_2O during the pretreatment process.

(b) Though many sites may have initially exchanged with the D_2O only 30-60% of the sites are capable of exchange with propylene due to steric considerations etc.

(c) The number of active sites appear to be decreased by doubling the antimony content of the catalyst.

Observation (2) suggests that the exchange reaction terminated when the active -OD sites became exhausted. Thus, an estimate of the number of active sites on the catalyst surface was obtained.

It has just been proposed that replacement of a number of labile surface hydroxyl groups, by deuteroyl groups, was responsible for the increased initial rate of exchange of propylene on D_2O pretreated catalysts. However, no account has yet been taken of the information that during the course of a propylene/ D_2O exchange reaction, over a D_2O pretreated catalyst, the loss of propylene from the gas phase was

only about 5% over 300 minutes. It may be, that D_2O pretreatment of the catalyst, in some way prevents the propylene polymerisation or oxidation products from blocking the active exchange sites on the catalyst surface. When propylene and D_2O are admitted together into the reaction vessel, there may be a competition between them for suitable sites on the catalyst. Thus, by pretreating the catalyst with D_2O prior to the reaction, the number of sites available for propylene poisoning are substantially reduced, resulting in a faster exchange reaction.

The results for propylene/ D_2O exchange over both non-treated and pretreated catalysts indicated clearly the following points:-

- (1) Only 5 of the 6 propylene hydrogen atoms are exchangeable.
- (2) The exchange occurs via a simple or stepwise mechanism.
- (3) The 5 propylene hydrogen atoms react at a similar rate.

The isobutene/ D_2O exchange reactions over both non-treated and pretreated catalysts produced results which were characteristically very similar in all but two respects to those obtained for propylene. The points of divergence being, that the rate of the exchange reaction was considerably faster for isobutene than for propylene and that all eight of the hydrogen atoms could be exchanged.

For the isobutene/ D_2O exchange reactions the following points were observed:-

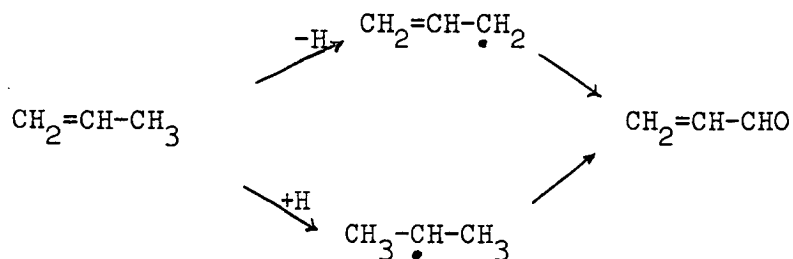
- (1) All 8 of the isobutene hydrogen atoms undergo exchange.
- (2) The exchange occurs via a simple or stepwise mechanism.
- (3) The 8 isobutene hydrogen atoms all react at the same rate.

The above evidence could support theories based on either a carbonium ion type of intermediate or an allylic intermediate. A carbanion intermediate theory is rejected on the grounds that replacement of the hydrogen atom on the central carbon atom of propylene, by a methyl group, would have destabilised the resulting intermediate, leading to a rate of exchange \leq the rate of exchange for propylene. Evidence from the literature supports the rejection of a carbanion type of intermediate⁽⁶⁶⁾.

The most likely reactive intermediates by which both propylene and isobutene could react and fulfil the above conditions are:-

- (1) Carbonium ion.
- (2) Allylic intermediate.
- (3) Isopropyl intermediate.

McCain et al⁽⁷⁸⁾ have shown that on a deuterated bismuth-molybdenum-oxide catalyst, propylene is oxidised to acrolein via a π -allyl as opposed to an isopropyl intermediate, the resulting acrolein containing no deuterium.

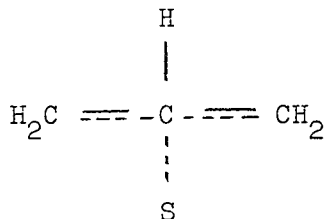


Bearing in mind the similarity in oxidation behaviour between the bismuth-molybdenum-oxide system and the tin-antimony-oxide system, the choice of intermediate lies between a carbonium ion or an allyl intermediate. Both

intermediates would permit exchange of all the hydrogen atoms of isobutene, but the hydrogen atom on the central carbon atom of propylene would not be replaced.

The infrared spectroscopic analysis results for the propylene/D₂O exchange reaction indicate clearly that the propylene/D₂O exchange reaction, over tin-antimony-oxide catalysts, proceeds via an allylic intermediate.

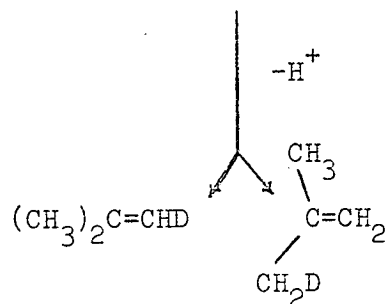
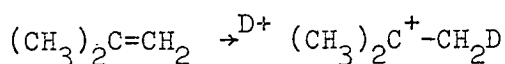
The allyl intermediate is most probably formed by the abstraction of an allylic hydrogen atom, possibly by a surface oxygen atom, to form a symmetrical allyl intermediate. Thus, the mechanism of exchange involves the reversible dissociative adsorption of propylene on the catalyst by splitting off an allylic hydrogen atom to form an allylic complex with a surface ion, s, possibly Sb^{s+}.



As can be seen the terminal carbon atoms of the allyl intermediate are identical, therefore, it is easy to understand why five of the six propylene hydrogen atoms are replaced with equal ease while the sixth, being located in a structurally unfavourable position, is not exchanged. It may be noted that uncertainty exists as to whether the initially abstracted hydrogen atom is lost as a proton or as a radical.

A detailed discussion of the proposed mechanism by which propylene interacts with the catalyst surface follows later in this chapter.

The experimental evidence and the relevant heats of formation of the intermediates⁽⁹²⁾ indicate that the isobutene/D₂O exchange reaction, over the same catalysts, is very likely to proceed via a tertiary carbonium ion intermediate:-



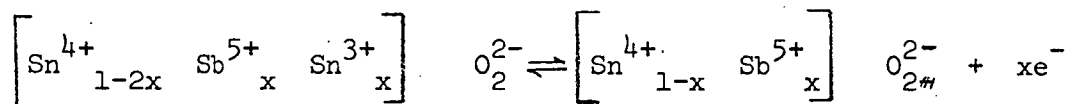
In agreement with the experimental results all eight hydrogen atoms are readily exchangeable in a stepwise manner, by this mechanism.

Figures 5.9 and 5.16 indicate that catalysts with compositions around 5 atom % Sb are the most active for both the propylene/D₂O and isobutene/D₂O exchange reactions. As has been shown, pretreatment of the catalysts with the respective olefins, reduces the activity of the catalyst to a somewhat similar value. Consideration of catalyst structure allied to catalytic activity may help to explain the catalytic activity pattern. With regard to the exchange reactions consideration need only be given to catalytic activity (measured by comparison of the initial rate constants) and not to selectivity which will be dealt with later.

Tin oxide by itself is a moderately active catalyst; however, antimony oxide remains essentially unreactive. This is in agreement with

the work of McCain⁽⁵²⁾, Grasselli⁽⁸⁵⁾, Wakabayashi⁽¹⁰¹⁾ and Belousov⁽¹⁰²⁾. It has been shown⁽⁵²⁾ that stannic oxide is a broad band n-type semiconductor and that conductivity is due to donor levels which arise from defects such as impurity cations and anion vacancies^(103,104). Antimony oxide on the other hand is a p-type semiconductor.

The addition of about 5 atom % Sb to tin oxide greatly increases the conductance, producing a semiconductor with a very low temperature coefficient. This behaviour has been observed previously⁽¹⁰³⁾ and is attributed to the substitution of Sb^{5+} for Sn^{4+} in the stannic oxide lattice, thus increasing the number of free electrons by the creation of Sn^{3+} ions equal in number of the added Sb^{5+} ions. The Sn^{3+} ions act as electron donors which on ionisation give free electrons and, therefore, cause a rise in the electrical conductivity:-



During catalyst preparation it is possible for a small amount of antimony to go into solid solution in the tin oxide, the exact amount being dependent upon the heat treatment temperature programme and duration. However, various estimates of atom % antimony going into solid solution average around 5%. The catalyst, therefore, consists of $\text{SnO}_2 + \text{Sb}$ solid solution, $\alpha\text{-Sb}_2\text{O}_4$ and minor amounts of $\beta\text{-Sb}_2\text{O}_4$. Experimentally, maximum catalytic activity occurs around the 5 atom % antimony composition. Therefore, the catalytically active component of the catalyst, for the exchange reactions, could be the $\text{SnO}_2 + \text{Sb}$ solid

solution phase. At an antimony oxide content exceeding the solubility limit, a system consisting of a solid solution, active for exchange and an insulating Sb_2O_4 matrix, inactive for exchange, exist. Thus at higher atom % Sb compositions we would expect the activity of the catalyst to fall off, due to a dilution of the active phase with the inert matrix, this behaviour pattern has in fact been observed.

For the propylene oxidation reactions, catalytic ~~activity~~^{activity}, taken as the specific first order rate constant for the disappearance of propylene, shows basically similar trends in relation to catalyst composition to those obtained for propylene/ D_2O and isobutene/ D_2O exchange. Consideration of the catalyst structure leads one to suggest that, once again, the catalytically active component of the catalyst, this time for propylene oxidation, could be the $\text{SnO}_2 + \text{Sb}$ solid solution phase. As before, at higher atom % Sb compositions the activity of the catalyst falls off gradually, in agreement with a dilution effect of the active phase by the non-active Sb_2O_4 matrix. However, though the rate of oxidation tends to decrease as the atom % Sb is increased so the specificity of the oxidation reaction towards acrolein, increases. The increase in specificity at higher atom % Sb concentrations is to be expected as antimony oxides by themselves are fairly non-reactive, but highly specific^(85,102). Therefore, as their concentration in the catalyst increases so does their moderating influence. It would appear that a successful industrial catalyst should consist of the highly active solid solution phase for rapid oxidation, combined with the moderating influence of the Sb_2O_4 matrix to give high specificity. This of course

neglects such factors as catalyst porosity, strength and lifetime properties.

The propylene oxidation results indicate that since the heterophase exchange reaction is not occurring, the lack of extensive ^{18}O incorporation into the oxidation products suggests that not only do oxide ions in the surface layer participate in the reaction, but also oxide ions in many subsurface layers. Consequently diffusion of oxygen from the surface into the bulk and vice versa must occur rapidly, thus permitting the ^{18}O to become equilibrated throughout a number of layers before reaction. Had the oxidation proceeded through a chemisorbed layer of oxygen only, then the products would have contained about 90% ^{18}O since nearly pure $^{18}\text{O}_2$ was used.

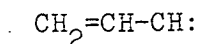
Confirmation of the reactivity of the surface and subsurface oxygen atoms was obtained by reacting propylene and $^{16}\text{O}_2$ over an $^{18}\text{O}_2$ pretreated catalyst. The only source of ^{18}O was now the ^{18}O which had become incorporated into the catalyst during the pretreatment exchange process. The results show clearly that the oxidation products did in fact contain ^{18}O , strongly suggesting that the ^{18}O was able to become at least partially equilibrated with the active oxygen atoms in the crystal lattice.

The initial rapid disappearance of propylene from the gas phase can only be attributed to the adsorption of propylene on the catalyst surface. The amount of propylene lost from the gas phase, about 10%, is in agreement with the amount of propylene lost from the gas phase during the propylene pretreatment process prior to a propylene/ D_2O exchange reaction. In both instances, carbon residue analysis conducted on the catalyst confirmed that carbon had been deposited on the catalyst

surface. Therefore, it was most likely that the catalyst surfaces were in a similar condition prior to their respective reactions. Direct comparison between the rate of propylene/D₂O exchange and the rate of propylene oxidation over similar catalyst surfaces can consequently be justified.

The Arrhenius data clearly indicates that the rates of exchange and oxidation and the corresponding energies of activation are comparable, temperature variation having been taken into account. This suggests that the common rate determining step for both the propylene/D₂O exchange reaction and the propylene oxidation reaction is the abstraction of an allylic hydrogen atom to form a symmetrical allyl intermediate. This proposal is in agreement with the work of Adams et al^(50,69), McCain et al⁽⁵²⁾, Grasselli et al⁽⁸⁵⁾, Voge et al⁽⁶⁵⁾, Sachtler^(67,68) and Peacock et al⁽⁵¹⁾.

The conclusion drawn from these results is that propylene oxidation proceeds via a symmetrical allyl intermediate, formed by the abstraction of an allylic hydrogen atom. The rate determining step is the abstraction of the allylic hydrogen. The oxidation reaction most probably proceeds further by the abstraction of a second hydrogen atom from either end of the symmetrical intermediate to form a highly reactive, hydrogen deficient intermediate possibly with a vinyl carbene structure^(59,60 and 85):-



Lattice oxygen then inserts into the C₃H₄ complex which after electronic rearrangement forms chemisorbed acrolein, which then desorbes.

Although the structural picture of the tin-antimony-oxide system has not been clearly defined, experimental evidence points to the necessity of having Sb^{5+} ions in an octahedral environment^(52,85) for the successful oxidation of propylene to acrolein (or ammoxidation to acrylonitrile). Antimony oxides by themselves are essentially non-reactive, but quite selective, whereas tin oxide appears to be moderately reactive but forms essentially complete oxidation products. Hence it is reasonable to suggest that the tin while stabilising the Sb^{5+} by structural means, also provides a path, via a redox reaction, for regeneration of the Sb^{5+} site once it has been reduced to a lower oxidation state in the course of the propylene oxidation reaction.

A number of mechanistic schemes involving successive reduction/oxidation cycles of the active catalyst site, combined with rapid lattice oxygen transfer, are possible. The structural position of the allylic intermediate on the active catalyst site is likewise open to question, as is the nature of the active oxygen species. If the tin-antimony-oxide catalyst structure essentially resembles the rutile structure, then the C_3H_5 symmetrical intermediate can occupy such a position that the terminal carbon atoms are symmetrically orientated with respect to the active oxygen atom⁽¹⁰⁵⁾. Such a situation could occur about one of the six equivalent, symmetrical oxygen atoms bonded both to an isolated antimony atom and to a tin atom, thus lending further support to the concept, that the activity centres round an antimony site.

The nature of the active oxygen species is in doubt since Schuit⁽¹⁰⁶⁾ has shown that for the conversion of butene to butadiene over bismuth-

-molybdenum-oxide catalysts a number of different active sites are involved. The overall oxidation reaction was shown to be a bifunctional process on a bifunctional catalyst. Grasselli⁽⁸⁵⁾ has likewise shown that different types of oxygen may exist for different oxidative functions.

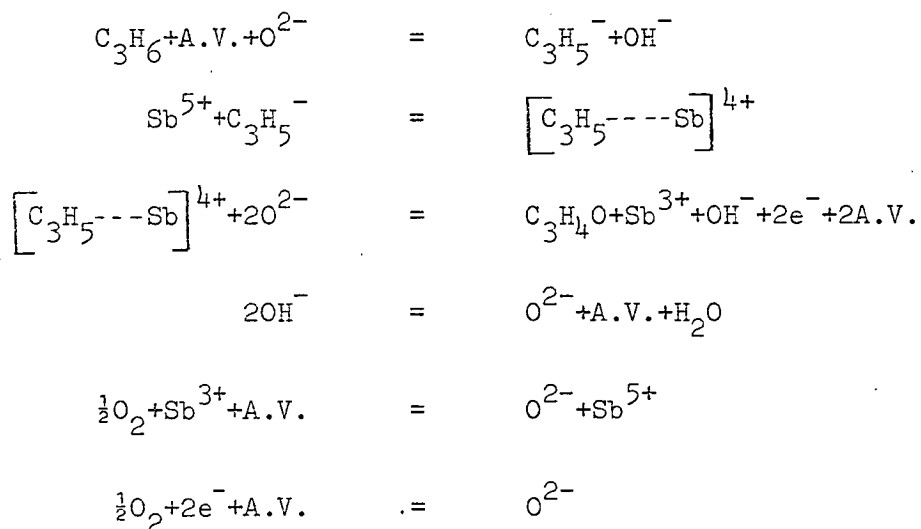
However, a possible mechanism for the propylene oxidation reaction, based on the experimental results and known catalyst structure, as discussed previously, can now be considered.

The catalyst activation procedure, which involved outgassing in vacuo at the reaction temperature for a number of hours, is likely to generate surface anion vacancies. Propylene then becomes chemisorbed at an anion vacancy and loses an allylic hydrogen atom, possibly as a proton, to a tin oxygen. Redox potential measurements⁽¹⁰⁷⁾ indicate that reduction/oxidation cycles are more likely to occur at an Sb^{5+} site than an Sn^{4+} site. This fact, in conjunction with the experimental data, suggests that an Sb^{5+} ion is likely to be the active centre.

Co-ordination of the allylic intermediate to an antimony ion results in reduction of Sb^{5+} . A second hydrogen abstraction from either end of the symmetrical allyl complex, probably effected by one of the equivalent lattice oxygen atoms surrounding the Sb atom, results in the formation of a highly hydrogen deficient C_3H_4 species. Loss of H_2O from the new complex creates an anion vacancy in the immediate vicinity of the complex, this vacancy can then be filled by an oxygen atom from the subsurface layers by rapid lattice oxygen transfer. The oxygen inserts into the C_3H_4 complex and after electronic rearrangement forms chemisorbed

acrolein which then desorbs, the anion vacancy consequently being regenerated. The loss of H_2O and oxygen insertion steps in the above mechanism could easily occur in the reverse order resulting in anion vacancy regeneration by loss of water.

The above mechanism is essentially similar to the mechanism proposed by McCain et al⁽⁵²⁾, the Sn^{4+} and Sn^{2+} species somehow being involved in the redox regeneration of Sb^{5+} .



where $[C_3H_5 \cdots Sb]^{4+}$ represents an allyl anion π bonded to Sb^{5+} and A.V. is an anion vacancy.

No evidence was found to substantiate the claims of Cant and Hall⁽⁷⁰⁾ and Keulks⁽⁷⁶⁾ et al, that an additional surface initiated homogeneous reaction was occurring in the post catalytic volume.

Such a reaction may possibly have escaped experimental detection, though propylene oxide formation would have been detected.

Propylene oxidation and ammoxidation reactions on bismuth-molybdenum-oxide catalysts appear to follow similar mechanistic routes^(50,66,69 and 80)

and bear close resemblance to the corresponding reactions on tin-antimony-oxide catalysts. The mechanism of oxidation comprises successive reaction of propylene with lattice oxygen, followed by replacement of oxide ions from gaseous oxygen⁽⁵¹⁾, rather than reaction of propylene with oxygen chemisorbed on the surface of a stoichiometric oxide. In the presence of ammonia the lattice oxygen reacts with NH_3 , possibly forming an NH group which then inserts into the C_3H_4 complex, to produce acrylonitrile.

Keulks⁽⁹³⁾ and Wragg et al⁽¹⁰⁸⁾, have proposed that the mechanism for the incorporation of oxygen into the oxidation products and into the catalyst, can be interpreted in terms of the layer structure proposed for the bismuth-molybdenum-oxide catalyst by Batist et al⁽¹⁰⁹⁾. Anion vacancies in the oxygen - boundary layers serve as active sites for propylene reactivity. In addition, the oxygen - boundary layers serve as the source of oxygen that is incorporated into the products. Reoxidation of these layers, by diffusion of O^{2-} ions from the bulk of the catalyst, as opposed to gas phase oxygen reoxidation appears to be favoured.

The flow system investigation of propylene oxidation was very valuable from the point of view that confirmation of the static investigation results was obtained, also that catalytic trends obtained by one type of investigation technique, could be usefully related to a different experimental system. The results obtained from both systems are in general agreement with the work published by Godin, McCain and Porter⁽⁵²⁾ relating to similar catalysts.

The results from the propylene/ $^{18}\text{O}_2$ investigation prove conclusively that the oxygen ions involved in the reaction, reach the active sites primarily by means of lattice oxygen transfer. Reoxidation of the depleted layers by diffusion of oxygen ions from the bulk of the catalyst, is preferred to gas phase oxygen regeneration. Gaseous oxygen is incorporated into the crystal lattice probably at some site other than the site for propylene adsorption.

The isotopic oxygen exchange results from Table 7.1 suggest that as a relatively high temperature, of around 773 K, is required for reaction then the isotopic exchange must proceed via a dissociative atomic mechanism, possibly involving only the surface layer of oxygen ions. The difference in reaction temperature required for propylene oxidation as opposed to isotopic oxygen exchange, suggests that the isotope exchange rate determining step may be the desorption step, in agreement with the findings of Winter⁽⁸⁷⁾ and Boreskov⁽⁹⁹⁾. The results also indicate that the rate of exchange varied according to the following order:-

$\text{SnO}_2 \approx 6.13 \text{ atom \% Sb} > 9.09 \text{ atom \% Sb} > 29.6 \text{ atom \% Sb} > 50 \text{ atom \% Sb}$
 $> \dots 75 \text{ and } 100 \text{ atom \% Sb.}$

The above order is somewhat similar to that obtained for propylene oxidation and for propylene/ D_2O exchange. However, as the atom % Sb content of the catalyst is increased the rate of isotopic oxygen exchange tends to fall off far more rapidly, than for the other reactions.

It may be proposed that a different type of oxygen is required to initiate and propagate the isotopic oxygen exchange reaction, than is necessary for propylene oxidation and that this oxygen tends to be associated more with the tin atoms than with the antimony atoms. Evidence to support these theories is forthcoming from the substantially higher temperature required for exchange and from the fact that the rate of exchange decreases substantially as the inert Sb_2O_4 matrix dilutes the active phase.

It was noted in section 7.5 that in a number of cases curvature of the $\log \frac{w-w_\infty}{w_0-w_\infty}$ against time plot tended to occur once the $K_{\text{equilibrium}}$ point (i.e. $K=4$) had been reached. This may be explained by considering that two or more types of active site exist, the first type being more active for isotopic oxygen exchange than the second. Supposing that the more active sites are occupied first, then while the first sites of similar energy are being occupied we would expect to obtain a linear plot. The exhaustion of the more active sites might then correspond to the $K_{\text{equilibrium}}$ point of the reaction. Further reaction then occurring on the less active sites would result in deviation of the linear first order plot. A further contributing factor may be that once the $K_{\text{equilibrium}}$ point has been reached then the nature of the surface reaction may alter in some way.

Comparison of the respective $2R^2+R^1$ and R^1+R^2 rate constants in Table 7.1 clearly indicates that over the tin oxide and 6.13 atom % Sb catalysts the isotopic oxygen exchange reaction proceeds via a dissociative atomic R^1 type mechanism⁽⁸⁷⁾. No distinction can be made between the various mechanistic routes by which the R^1 type of mechanism may proceed.

The various routes have been described in detail in section 7.3. For the remaining catalysts no clear cut distinction can be made between the various mechanisms, although the indications are that as the atom % antimony in the catalyst is increased so the mechanistic route changes from R^1 to R^2 . It may be that at the higher temperatures required for catalysts richer in antimony to react, then homomolecular exchange plays an increasingly important part.

In conclusion it can be said that the mechanistic route by which isotopic oxygen exchange occurs over the range of tin-antimony-oxide catalysts must be essentially different from the mechanism operative during propylene oxidation or propylene/ D_2O exchange over the same catalysts.

Conclusion

The main conclusions to be drawn from the present work on tin-antimony-oxide catalysts can be summarised as follows. The propylene/D₂O exchange reaction and the propylene oxidation reaction both occur via a common, symmetrical allyl intermediate. The rate determining step is the abstraction of an allylic hydrogen atom, from the propylene molecule, to form the allylic intermediate. The isobutene/D₂O exchange reaction most probably proceeds via a tertiary carbonium ion intermediate.

The propylene/D₂O exchange reaction proceeds via the allylic intermediate, to give simple or stepwise exchange of five of the six propylene hydrogen atoms. On the other hand, the propylene oxidation reaction proceeds past the allylic intermediate stage, by the abstraction of a second hydrogen atom from either end of the symmetrical intermediate, to form a highly reactive, hydrogen deficient species. Lattice oxygen then inserts into the C₃H₄ complex to form chemisorbed acrolein, which then desorbs. Reoxidation of the reduced sites is then effected by lattice oxygen transfer from the bulk of the catalyst. Gaseous oxygen is incorporated into the crystal lattice at some site other than the site for propylene adsorption.

Isotopic oxygen exchange appears to proceed via a dissociative atomic R¹ or R² type of mechanism, the rate determining step most probably being the desorption of oxygen from the catalyst surface.

Catalytic activity, for all reactions, appears greatest at the low atom % antimony compositions. This fact can be reconciled with the formation of a solid solution phase, in which antimony ions have replaced a number of tin ions in the tin oxide structure. It is therefore suggested that the catalytically active component of the catalysts is in fact the $\text{SnO}_2 + \text{Sb}_2\text{O}_4$ solid solution phase. The observed reaction rates and selectivities on different catalyst compositions are dependent on the moderating influence of the varying amounts of Sb_2O_4 matrix.

Future work on this system might beneficially be directed towards an investigation of the behaviour of the intermediate species on the catalyst surface, under a variety of catalyst environmental conditions. Such an investigation might be accomplished by subjecting the suitably conditioned catalysts to a rigorous E.S.R. and Mossbauer spectroscopic examination.

FORTRAN IV G LEVEL 20

MAIN

DATE = 72305

13/07/42

PA

```
0001      INTFGR S,C,0
0002      DATA BLANK/' '/
0003      DIMENSION P(40),FH(10),FD(10),PER(20),D(20),KK(7),NN(20),NH(8),
          WND(8)
0004      READ(5,100) ISETS
0005      100 FORMAT(I2)
0006      ONEC=0.010806
0007      ONEQ=0.00039093
0008      ONEO=0.00016003
0009      TWCC=0.00005838
0010      TWOO=0.0000000764
0011      TWOD=0.0000000128
0012      CANDO=0.0000042242
0013      CANDD=0.0000017292
0014      DANDO=0.0000000626
0015      BIGO=0.0020048
0016      READ(5,101) C,N,O,M
0017      101 FORMAT(4I3)
0018      K=N+M+1
0019      IPEAK=N+M+2
0020      S=M+1
0021      NN(1)=N
0022      DO 47 I=2,N
0023      47 NN(I)=NN(I-1)*(N-I+1)
0024      READ(5,105) (FH(IFRAG),IFRAG=1,S)
0025      105 FORMAT(10F6.4)
0026      READ(5,105) (FD(IFRAG),IFRAG=1,S)
0027      DO 56 INOS=1,ISETS
0028      READ(5,103) TIME
0029      103 FORMAT(F6.1)
0030      READ(5,104) (P(J),J=1,K)
0031      104 FORMAT(13F6.1)
0032      WRITE(6,37)
0033      37 FORMAT('0',///3X,'LIGHT HYDROCARBON FRAGMENTATION PATTERN')
0034      WRITE(6,1003) (BLANK,LULU=1,M)
0035      1003 FORMAT('0',2X,6HPARENT,2X,A1,'-1H',4X,A1,'-2H',4X,A1,'-3H',4X,A1,'
          W-4H',4X,A1,'-5H',4X,A1,'-6H',4X,A1,'-7H',4X)
          WRITE(6,102) (FH(IFRAG),IFRAG=1,S)
0036      102 FORMAT('0',8F8.4)
0037      WRITE(6,38)
0038      38 FORMAT('0',3X,'HEAVY HYDROCARBON FRAGMENTATION PATTERN')
0039      WRITE(6,1003) (BLANK,LULU=1,M)
0040      WRITE(6,102) (FD(IFRAG),IFRAG=1,S)
0041      WRITE(6,33)
0042      33 FORMAT('0',10X,25HEXPERIMENTAL PEAK HEIGHTS)
0043      DO 123 KZ=1,7
0044      123 KK(KZ)=8-KZ
          NHIGH=8-M
          WRITE(6,1002) (BLANK,KK(KZ),KZ=NHIGH,7)
0045      1002 FORMAT('0',2X,A1,'D-',I1,4X,A1,'D-',I1,4X,A1,'D-',I1,4X,A1,'D-',
          W I1,4X,A1,'D-',I1,4X,A1,'D-',I1,4X,A1,'D-',I1,4X)
          WRITE(6,25) (P(J),J=1,M)
0046      25 FORMAT('0',10F8.1)
          WRITE(6,1001) (BLANK,LULU=1,N)
0047      1001 FORMAT('0',4X,'D0',5X,A1,'D1',5X,A1,'D2',5X,A1,'D3',5X,A1,'D4',5X,
          W A1,'D5',5X,A1,'D6',5X,A1,'D7',5X,A1,'D8',5X,A1,'D9',5X,A1,'D10',5X
```

```

W,A1,'D11',5X,A1,'D12')
0053 WRITE (6,25)(P(J),J=S,K)
0054 DO 3 J=1,K
0055 IF(P(J).LT.0.0)GOTO3
0056 L=IABS(J-S)
0057 IF(L.EQ.N) GO TO 3
0058 SIC=ONEC*C+ONEO*O+ONED*(N-L)
0059 P(J+1)=P(J+1)-SIC*P(J)
0060 IF (L.GT.N-2) GO TO 3
0061 DIC=TWOC*C*(C-1)+TWOO*O*(O-1)+TWOD*(N-L)*(N-L-1)+CANDO*C*O+CANDD
W*C*(N-L)+DANDO*O*(N-L)+BIGD*O
0062 P(J+2)=P(J+2)-DIC*P(J)
0063 3 CONTINUE
0064 WRITE(6,35)
0065 35 FORMAT('0',10X,34HPEAK HEIGHTS CORRECTED FOR ISOTOPE,2X)
0066 DO 124 KZ=1,7
0067 124 KK(KZ)=8-KZ
0068 NHIGH=8-M
0069 WRITE (6,1002) (BLANK, KK(KZ), KZ=NHIGH, 7)
0070 WRITE(6,25) (P(J),J=1,M)
0071 WRITE(6,1001) (BLANK,LULU=1,N)
0072 WRITE (6,25)(P(J),J=S,K)
0073 GAMMA=1.0000
0074 PI=1.0000
0075 GO TO 1375
0076 NCOM=NN(2)/2

0077 NPERM=NN(3)/6
0078 D(N-2)=NCOM*(P(K-1))**2/(P(K)*N**2)
0079 D(N-3)=N*NPERM*(D(N-2))**2/(P(K-1)*NCOM**2)
0080 FLAW=(P(K-2)-D(N-2)-FD(2)*P(K))/P(K-1)
0081 GAMMA=(FLAW/(FH(2)/N))**(1.0/(N-1))
0082 FLEW=2*FH(2)/N*GAMMA**(N-2)
0083 FLOW=(P(K-3)-D(N-3)-FLEW*D(N-2))/P(K-1)
0084 PI=FLOW/(FD(2)*(N-1)/N)
0085 1375 CONTINUE
0086 WRITE (6,2121)GAMMA,PI
0087 2121 FORMAT('0',6X,6HGAMMA=,F7.4,8X,3HPI=,F7.4,2X)
0088 DO 79 IFRAG=1,M
0089 FH(IFRAG)=FH(IFRAG+1)
0090 FD(IFRAG)=FD(IFRAG+1)
0091 79 CONTINUE
0092 DO 4 I=1,IPEAK
0093 J=IPEAK-I
0094 IF(J.EQ.M) GO TO 45
0095 L=J-S
0096 IF (P(J).LT.0.0) GO TO 4
0097 NH(1)=1
0098 ND(1)=1
0099 NH(2)=N-L
0100 ND(2)=L
0101 IF(S.LT.3) GO TO 901
0102 DO 46 IVY=3,S
0103 NH(IVY)=NH(IVY-1)*(NH(2)-IVY+2)
0104 46 ND(IVY)=ND(IVY-1)*(L-IVY+2)

```

```

0105      901 CONTINUE
0106      ZH=GAMMA**L
0107      ZD=PI**(N-L)
0108      DO 4 NPL=1,M
0109      NB=NPL+1
0110      DO 4 NA=1,NB
0111      NHL=NA-1
0112      NDL=NPL-NHL
0113      NWAYS=NPL
0114      IF(NHL.LT.2) GO TO 902
0115      DO 48 IRIS=2,NHL
0116      48 NWAYS=NWAYS*(NPL-IRIS+1)/IRIS
0117      902 CONTINUE
0118      CORR=NWAYS*(NHL*FH(NPL)+NDL*FD(NPL))*ND(NDL+1)*NH(NHL+1)/
      W(NN(NPL)*NPL)*ZD**NDL*ZH**NHL
      P(J-NHL-2*NDL)=P(J-NHL-2*NDL)-CORR*P(J)
0119      4 CONTINUE
0120      45 WRITE (6,300)
0121      300 FORMAT ('0',10X,22HCORRECTED PEAK HEIGHTS)
0122      DO 125 KZ=1,7
0123      125 KK(KZ)=8-KZ
0124      NHIGH=8-M
0125      WRITE(6,1002) (BLANK, KK(KZ), KZ=NHIGH,7)
0126      WRITE(6,25) (P(J), J=1,M)
0127      WRITE(6,1001) (BLANK, LULU=1,N)
0128      WRITE (6,25) (P(J), J=S,K)
0129      DO 82 NHIGH=1,M
0130      IFRAG=S-NHIGH
0131      FD(IFRAG+1)=FD(IFRAG)
0132      82 FH(IFRAG+1)=FH(IFRAG)
0133      FD(1)=1.0000
0134      FH(1)=1.0000
0135      TOTAL=0.0
0136      DO 60 J=S,K
0137      IF (P(J).LT.0.0) GO TO 60
0138      TOTAL=TOTAL+P(J)
0139      60 CONTINUE
0140      WRITE (6,400)
0141      400 FORMAT ('0',10X, 30HPERCENTAGE OF ISOTOPIC SPECIES)
0142      WRITE(6,1001) (BLANK, LULU=1,N)
0143      DO 810 J=S,K
0144      810 PER(J)=P(J)*100/TOTAL
0145      WRITE(6,25) (PER(J), J=S,K)
0146      PHI=0.0
0147      DO 80 J=S,K
0148      L=J-S
0149      IF(PER(J).LT.0.0) GO TO 80
0150      PHI=PHI+L*PER(J)
0151      80 CONTINUE
0152      WRITE(6,410) TIME, TOTAL, PHI
0153      410 FORMAT('0',9X,4HTIME,9X,5HTOTAL,9X,3HPHI/F14.1,F15.2,F13.2)
0154      WRITE(6,34) PHI
0155      34 FORMAT('0',10X,31HBINOMIAL DISTRIBUTION WITH PHI=,F9.2,2X)
0156      YY=PHI/(100*N)
0157      XX=1.0000-YY
0158      D(1)=100*XX**N
0159

```

```
0160         JEAN=N+1
0161         DO 59 JIM=2,JEAN
0162           59 D(JIM)=D(JIM-1)*(JEAN-JIM+1)*YY/(XX*(JIM-1))
0163           WRITE(6,1001) (BLANK,LULU=1,N)
0164           WRITE(6,25) (D(JIM),JIM=1,JEAN)
0165           56 CONTINUE
0166     3000   STOP
0167         END
```

REFERENCES

1. Berzelius, J., Jahresber. Chem., 15, 237(1836).
2. Van Marum, J., J. der Phys., 3, 359(1796).
3. Kirchhoff, G.R., Schweigger's Journal, 4, 108(1812).
4. Thenard, J., Ann. Chim. Phys., 2, 314(1818).
5. Davy, H., Phil. Trans., 7, 77(1817).
6. Dobereiner, J., Schweigger's Journal, 34, 91(1822).
7. Mitscherlich, E., Pogg. Ann., 31, 273(1834).
8. Ostwald, W., Physik Z., 3, 313(1902).
9. Faraday, M., Phil. Trans., 114, 55(1834).
10. Sabatier, P., La Catalyse En Chemie Organique (Paris and Liege, 1913).
11. Langmuir, I., Phys. Rev., 6, 79(1915).
12. Brunauer, S., "The Physical Adsorption of Gases and Vapours", (O.U.P., Lond., Princeton U.P., Princeton, 1943).
13. Scholter, J.J.F. and Zwietering, P., Actes Congr. Intern. Catalyse, 2, Paris, 1960, 389 (Ed. Technip., Paris, 1961).
14. Brunauer, S., Emmett, P.H. and Teller, E., J. Amer. Chem. Soc., 60, 309(1938).
15. Shull, C.G., J. Amer. Chem. Soc., 70, 1405(1948).
16. Wheeler, A., Adv. In Catalysis, 3, 250(1951).
17. Hayward, D.O. and Trapnell, B.M.W., "Chemisorption" (Butterworth, Lond., 1964).
18. Roberts, J.K., Proc. Roy. Soc., A152, 445(1935).

19. Gundry, P.M. and Tompkins, F.C., *Quart. Rev.*, 14, 257(1960).
20. Eischens, R.P. and Pliskin, W.A., *Adv. In Catalysis*, 10, 1(1958).
21. Cornaz, P.F., Van Hooff, J.H.C., Pluijm, F.J. and Schuit, G.C.A.,
Disc. Farad. Soc., 41, 290(1966).
22. MacRae, A.U., *Science*, 139, 379(1963).
23. Kummer, J.T. and Emmett, P.H., *J. Chem. Phys.*, 19, 289(1951).
24. Hinshelwood, C.N., "The Kinetics of Chemical Change" (Clarendon
Press, Oxford, 1940).
25. Laidler, K.J., "Catalysis", Ed. Emmett, P.H., (Reinhold, New
York, 1954).
26. Rideal, E.K., Sabatier Lecture: *J. Soc. Chem. Ind.*, 62, 335(1943).
27. Eley, D.D., *Quart. Rev.*, 3, 209(1949).
28. Bond, G.C., "Catalysis By Metals", (Academic Press, Lond., 1962).
29. Kemball, C., *Adv. In Catalysis*, 11, 223(1959).
30. Kemball, C., *Proc. Chem. Soc.*, 264(1960).
31. Taylor, T.I., *Catalysis*, 5, 257(1957), (Reinhold, New York,
Ed. Emmett, P.H.).
32. Anderson, J.R., *Rev. Pure and Appl. Chem.*, 7, 165(1957).
33. Blyholder, G., "Experimental Methods In Catalytic Research", (Ed.
Anderson, R.B., Academic Press, London and New York, 1968).
34. Kokes, R.J., "Experimental Methods In Catalytic Research", (Ed.
Anderson, R.B., Academic Press, London and New York, 1968).
35. Bond, G.C. and Wells, P.B., *Adv. In Catalysis*, 15, 92(1964).
36. Siegel, S., *Adv. In Catalysis*, 16, 124(1966).

37. Stone, F.S., "Chemistry Of The Solid State", Chap. 15, (Ed. Garner, W.E., Butterworths, London, 1955).
38. Pauling, L., Proc. Roy. Soc., A196, 343(1949).
39. Coupar, A. and Eley, D.D., Disc. Farad. Soc., 8, 172(1950).
40. Dowden, D.A. and Reynolds, P., Disc. Farad. Soc., 8, 184(1950).
41. Dowden, D.A. and Wells, D., Actes Congr. Intern. Catalyse, 2, Paris, 2, 1499, 1960.
42. Wilson, A.H., "Semiconductors and Metals", (Cambridge Univ. Press, 1939).
43. Hauffe, K., Adv. In Catalysis, 7, 213(1955).
44. Fensham, P.J., Quart. Rev., 11, 227(1957).
45. Volkenstein, F.F., "The Electronic Theory Of Catalysis On Semiconductors", (Pergamon Press, Oxford, 1963).
46. Dowden, D.A., MacKenzie, N. and Trapnell, B.M.W., Proc. Roy. Soc., A237, 245(1956).
47. Wood, B.J., Wise, H. and Yolles, R.S., J. Catalysis, 15, 355(1969).
48. Hearne, G.W. and Adams, M.L., U.S. Patent 2, 451, 485(1948), to Shell Development Co.
49. Veatch, F., Callahan, J.L., Millberger, E.C. and Forman, R.W., 2nd Actes Intern. Congr. Catalyse, Paris, 1960, Vol. II, p. 2647. Editions Technip., Paris, 1961.
50. Adams, C.R. and Jennings, T.J., J. Catalysis, 3, 549(1964).
51. Peacock, J.M., Parker, A.J., Ashmore, P.G. and Hockey, J.A., J. Catalysis, 15, 373, 379, 387, 398(1969).

52. Godin, G.W., McCain, C.C. and Porter, E.A., 4th Intern. Congr. On Catalysis, Moscow (1968), paper 20.
53. Idol, J.D., Jr., U.S. Patent 2, 904, 580(1959), to Standard Oil (Ohio).
54. Keiser, K., Batist, Ph.A. and Schuit, G.C.A., J. Catalysis, 15, 256(1969).
55. Batist, Ph.A., Prette, H.J. and Schuit, G.C.A., J. Catalysis, 15, 267(1969).
56. Beynon, J.H., "Mass Spectrometry And Its Applications To Organic Chemistry", (Elsevier, London), p.424(1960).
57. Jagers, A.J., Ph.D. Thesis, University of Edinburgh, (1970).
58. Kemball, C., Proc. Roy. Soc., A214, 413(1952).
59. Matsen, F.A. and Franklin, J.L., J. Amer. Chem. Soc., 72, 3334(1950).
60. Harper, R.J., Siegel, S. and Kemball, C., J. Catalysis, 6, 72(1966).
61. Margolis, L.Ya., Advan. Catalysis, 14, 429(1963).
62. Sampson, R.J. and Shooter, D., "Oxidation And Combustion Reviews", (C.F.H. Tipper, Ed.), Vol. I, p.223, Elsevier, Amsterdam, 1965.
63. Voge, H.H. and Adams, C.R., Advan. In Catalysis, 17, 151(1967).
64. Sachtler, W.M.H., Catalysis Rev., 4, 27(1970).
65. Voge, H.H., Wagner, C.D. and Stevenson, D.P., J. Catalysis, 2, 58(1963).
66. Adams, C.R., Proc. 3rd Intern. Congr. On Catalysis, Amsterdam, 1964; North-Holland, Amsterdam, 1, 240(1965).
67. Sachtler, W.M.H., Rec. Trav. Chim., 82, 243(1963).
68. Sachtler, W.M.H. and de Boer, N.H., Proc. 3rd Intern. Congr. On Catalysis, Amsterdam, 1964; North-Holland Publ., Amsterdam, 1, 252(1965).

69. Adams, C.R. and Jennings, T.J., *J. Catalysis*, 2, 63(1963).
70. Cant, N.W. and Hall, W.K., *J. Phys. Chem.*, 75, 2914(1971).
71. Cant, N.W. and Hall, W.K., *J. Catalysis*, 22, 310(1971).
72. McCain, C.C. and Godin, G.W., *Nature*, 202, 692(1964).
73. Keulks, G.W., Rosynek, M.P. and Daniel, C., *Ind. Eng. Chem. Prod. Res. Develop.*, 10, 138(1971).
74. Friedli, H.R., Hart, P.J. and Vrieland, G.E., *Amer. Chem. Soc., Div. Petrol. Chem., Prepr.*, 14, C70(1969).
75. Margolis, L.Y., *J. Catalysis*, 21, 93(1971).
76. Keulks, G.W. and Daniel, C., *J. Catalysis*, 24, 529(1972).
77. Buiten, J., *J. Catalysis*, 13, 373(1969).
78. McCain, C.C., Gough, G. and Godin, G., *Nature*, 198, 989(1963).
79. Batist, Ph.A., Kapteijns, C.J., Lippens, B.C. and Schuit, G.C.A., *J. Catalysis*, 7, 33(1967).
80. Hydrocarbon Processing, *Petrochemical Handbook*, 46, 140(1967).
81. Nier, A.D., *Anal. Chem.*, 20, 188(1948).
82. Halsted, R.E. and Nier, A.D., *Rev. Sci. Instrum.*, 21, 1019(1950).
83. Kemball, C., *Proc. Roy. Soc.*, A207, 539(1951).
84. Barnard, G.P., "Modern Mass Spectrometry", (The Institute Of Physics, London), p.112.
85. Grasselli, R.K. and Suresh, D.D., *J. Catalysis*, 25, 273(1972).
86. Lake, I.J.S. and Kemball, C., *Trans. Farad. Soc.*, 63, 2535(1967).
87. Winter, E.R.S., *J. Chem. Soc. (A)*, 2889(1968).
88. Evans, A.G., "The Reactions Of Organic Halides In Solution", 15, (1946), Manchester University Press.

89. Hirota, K. and Hironaka, Y., Bull. Chem. Soc. Japan, 37,
535(1964).
90. Farina, M. and Peraldo, M., Gazz. Chem. Ital., 90, 973(1960).
91. Norris, W.P., J. Org. Chem., 24, 1579(1959).
92. McCosh, R., Ph.D. Thesis, University of Edinburgh, (1968).
93. Keulks, G.W., J. Catalysis, 19, 232(1970).
94. Winter, E.R.S., Disc. Farad. Soc., 8, 231(1950).
95. Klier, K., Novakova, J. and Jiru, P., J. Catalysis, 2, 479(1963).
96. Winter, E.R.S., Adv. Catalysis, 10, 196(1958).
97. Boreskov, G.K., Adv. Catalysis, 15, 285(1964).
98. Novakova, J., Cat. Reviews, 4, 77(1971).
99. Sokolovskii, V.D., Sazonov, L.A. and Boreskov, G.K., Izvest.
Sibirsk. Otdel. Akad. Nauk. S.S.S.R., Inst. Katal., 1, 158(1965).
100. Gorgoraki, V.I., Boreskov, G.K., Kasatkina, L.A. and
Sokolovskii, V.D., Kinetika i Kataliz, 5, 120(1964).
101. Wakabayashi, K., Kamiya, Y. and Ohta, N., Bull. Chem. Soc. Japan,
40, 2172(1967).
102. Belousov, V.M. and Gershingorina, A.V., Kinetika i Kataliz.,
12, 614(1971).
103. Marley, J.L. and Dockerty, R.C., Phys. Rev., 140A, 304(1965).
104. Loch, L.D., J. Can. Ceram. Soc., 158(1964).
105. Matsuura, I. and Schuit, G.C.A., J. Catalysis, 25, 314(1972).
106. Matsuura, I. and Schuit, G.C.A., J. Catalysis, 20, 19(1971).
107. Handbook Of Chemistry and Physics, 48th Edition, Published By
The Chemical Rubber Co., (1967).
108. Wragg, R.D., Ashmore, P.G. and Hockey, J.A., J. Catalysis, 22,
49(1971).

109. Batist, Ph.A., Der Kinderen, A.H.W.M., Leeuwenburgh, Y., Metz, F.A.M.G. and Schuit, G.C.A., *J. Catalysis*, 12, 45(1968).
110. Morita, N. and Titani, T., *Bull. Chem. Soc. Japan*, 15, 1(1940).
111. Godin, G.W. and McCain, C.C., *International Symposium on Catalytic Oxidation*, Imperial College, London, 8th-9th July (1970).

ABSTRACT OF THESIS

Name of Candidate JAMES REDPATH CHRISTIE
Address 35 GROATHILL ROAD SOUTH, EDINBURGH, EH4 2LS.
Degree DOCTOR OF PHILOSOPHY Date OCTOBER, 1972.
Title of Thesis THE CHARACTERISATION OF OXIDE CATALYSTS BY INVESTIGATIONS
ON EXCHANGE REACTIONS.

The catalytic oxidation of propylene to form acrolein, over a range of tin-antimony-oxide catalysts, has been investigated by a number of physical techniques including isotopic exchange and oxidation. Propylene oxidation reactions and exchange reactions of propylene/D₂O, isobutene/D₂O and ¹⁶O₂/¹⁸O₂, over the catalysts, have been studied in a static system. The results of a kinetic study at reaction temperatures between 373 and 873 K are reported and possible reaction mechanisms are discussed. The propylene-d₁ species formed in the C₃H₆/D₂O reaction is shown by I.R. absorption measurements to be CH₂D-CH=CH₂.

The propylene/D₂O exchange reaction and the propylene oxidation reaction both occur with very similar rate constants via a common, symmetrical allyl intermediate. The rate determining step is the abstraction of an allylic hydrogen atom, from the propylene molecule, to form the allylic intermediate. The isobutene/D₂O exchange reaction most probably proceeds via a tertiary carbonium ion intermediate.

The propylene/D₂O exchange reaction proceeds via the allylic intermediate, to give simple or stepwise exchange of five of the six propylene hydrogen atoms. On the other hand, the propylene oxidation reaction proceeds past the allylic intermediate stage, by the abstraction of a second hydrogen atom from either end of the symmetrical intermediate, to form a highly reactive, hydrogen deficient species. Lattice oxygen then inserts into the C₃H₄ complex to form chemisorbed acrolein, which then desorbs. Reoxidation of the reduced site is then effected by lattice oxygen transfer from the bulk of the catalyst. Gaseous oxygen is incorporated into the crystal lattice at some site other than

cont/d...

Use other side if necessary.

cont/d...

the site for propylene adsorption.

Isotopic oxygen exchange appears to proceed via a dissociative atomic R^1 or R^2 type of mechanism, the rate determining step most probably being the desorption of oxygen from the catalyst surface.

Catalytic activity, for all reactions, appears greatest at the low atom % antimony compositions. This fact can be reconciled with the formation of a solid solution phase, in which antimony ions have replaced a number of tin ions in the tin oxide structure. It is therefore suggested that the catalytically active component of the catalysts is in fact the $\text{SnO}_2 + \text{Sb}_2\text{O}_4$ solid solution phase. The observed reaction rates and selectivities on different catalyst compositions are dependent on the moderating influence of the varying amounts of Sb_2O_4 matrix.