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COMPETITIVE CHLORINATION OF
UNSATURATED COMPOUNDS

by

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ABSTRACT OF THESIS

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Title of Thesis Competitive Chlorination of Unsaturated Compounds.

The competitive technique has previously been used to evaluate the Arrhenius parameters for the reaction



, where R = alkyl radical. In order to extend this technique to study the elementary reaction



, where A = olefine, it is necessary to have precise information about the mechanism of the chlorination of olefines.

The available literature on olefine chlorination has been reviewed and it is concluded that the mechanism is uncertain and that the Arrhenius parameters for reaction 2. are, therefore, unreliable.

The competitive chlorinations of cis and of trans dichloroethylene against propane have been studied and evidence obtained that the radical formed in reaction 2. is an energetic or "hot" radical which can decompose thus:

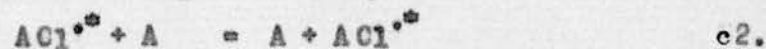


Alternatively, the radical may be collisionally deactivated:



Cis dichloroethylene, trans dichloroethylene, propane and carbon dioxide all deactivate the radical, but require about twice as many collisions as chlorine does to do so.

Atom exchange reactions of the type



do not occur.

The rate constant for the unimolecular decomposition of the hot radical differs slightly for the radicals formed from cis dichloroethylene and from trans dichloroethylene, suggesting that they differ in energy. The differences are small, however, and in both cases lifetime of the radical decreases from 5×10^{-10} sec. at $35^{\circ}C$ to 3×10^{-10} secs. at $132.5^{\circ}C$. The literature on hot radicals and molecules has been briefly reviewed.

Kinetic /

Kinetic expressions have been developed which allowed the Arrhenius parameters for the addition of a chlorine atom to cis and trans dichloroethylene to be obtained:

Cis dichloroethylene:

$$A_2 = 8.0 \pm 2.2 \times 10^{10} \text{ l.mole}^{-1} \text{ sec.}^{-1}, E_2 = 190 \pm 250 \text{ cal.mole}^{-1}.$$

Trans dichloroethylene:

$$A_2 = 3.0 \pm 0.7 \times 10^{10} \text{ l.mole}^{-1} \text{ sec.}^{-1}, E_2 = -170 \pm 230 \text{ cal.mole}^{-1}.$$

These results have been discussed in relation to the other values available for ethylene and the chloroethylenes.

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ABBREVIATIONS

The following abbreviations have been used in the text :-

PrH	Propane
iPrCl	iso-Propyl Chloride
nPrCl	n-Propyl Chloride
TCE	1,1,2,2 - Tetrachloroethane
DCE	1,2 - Dichloroethylene
CBE	1 - Chloro, 2 - Bromo-Ethylene
DBE	1,2 - Dibromoethylene

With respect to the 1,2-disubstituted ethylenes, the letters c and t refer to the cis and trans isomers, respectively, and the letter i is used when either cis and/or trans is intended.

The letter A is used to indicate olefine and ACl^* and ACl_2 then have their obvious significance.

PREFACE

In order to obtain the rate constants and Arrhenius parameters for the elementary reactions involved, by studying a free radical chain reaction it is essential to have a precise knowledge of the mechanism. The mechanism of the chlorination of hydrogen and the saturated aliphatic hydrocarbons and the Arrhenius parameters for the reaction



are now well established, but the mechanism of the chlorination of olefines is less well understood and the rate constants and Arrhenius parameters for the reaction



correspondingly less reliable.

The present work was aimed at resolving this ambiguity and a study of the competitive chlorination of cis and of trans dichloroethylene against propane was chosen as being particularly suitable for this purpose.

CHAPTER I.

I N T R O D U C T I O N

1. General:

Halogenation reactions have played an important role in the development of chemical kinetics. The first comprehensive study of the kinetics of a gas phase reaction was that of Bodenstein¹ (1894-99) on the formation of hydrogen iodide from hydrogen and iodine. He also studied the reverse reaction and the equilibrium constant and was able to show that both forward and reverse reactions obey a simple second order rate law. From similar work on the hydrogen/bromine system Bodenstein and Lind² (1907) derived an empirical rate expression that was much more complex and it was not until 1919 that Christiansen³, Herzfeld⁴ and Polanyi⁵ independently interpreted this expression in terms of the now well known bromine atom scheme. They were the first to apply the steady-state treatment to a complex reaction mechanism and show that it led to the empirical rate equation.

The reaction between hydrogen and chlorine has probably been more widely studied than any other chemical reaction. Much of the early data was collected by Bodenstein⁶ who proposed (1913) an ionic chain mechanism to explain the high quantum yield. In 1918 Nernst⁷ suggested an atomic chain mechanism and in 1923 Marshall and Taylor⁸ provided support for this idea by showing that when hydrogen atoms were introduced into a mixture of hydrogen and chlorine the hydrogen chloride formed was greatly in excess of the quantity of hydrogen atoms introduced. Introduction of chlorine atoms into the system was also shown to initiate a chain reaction^{9,10}.

Evidence for free methyl and ethyl radicals was obtained by Paneth and co-workers¹¹ and Taylor and Jones¹² showed that ethyl radicals, obtained by decomposing diethyl mercury, induced the polymerisation of ethylene. Thus, by 1930, the concept of a chain mechanism involving free atom and/or free radical chain centres was well established and the chlorination,¹³ oxidation¹⁴ and thermal decomposition¹⁵ of simple organic molecules in the gas phase were all shown to be free radical chain reactions¹⁶. The general approach was to study the overall kinetics, frequently by following pressure changes in the system, and then to postulate a plausible reaction mechanism from which the observed kinetic law could be obtained by applying the steady state treatment.

The application of quantum mechanics to the problem of calculating the activation energy of a reaction^{17,18} and the development of the transition state theory¹⁹ stimulated efforts to determine rate constants of elementary reactions but the experimental limitations were considerable and, although Arrhenius parameters were obtained for a number of reactions, Steacie commented in 1942 "that no single investigation of an elementary reaction has ever been made which is free from ambiguity"²⁰. Subsequently, the application of the kinetic techniques of competing reactions²¹ and intermittent illumination²², the introduction of flash photolysis²³ and shock waves²⁴ as means of producing a high concentration of radicals and the use of mass spectrometry²⁵, gas chromatography²⁶ and electron resonance spectroscopy²⁷ as analytical tools have enabled our knowledge of elementary rate constants to be greatly extended. Rate constants of about a hundred elementary reactions occurring in photo-chlorination systems are now known and attempts have been made to correlate the corresponding Arrhenius parameters with the values obtained by calculation from the transition state theory²⁸.

2. The Theory of Rate Processes¹⁹

In this section the transition state theory of chemical reactions will be outlined and its relationship to the collision theory of reaction rates and the Arrhenius equation briefly discussed.

The Arrhenius Equation: Arguing on the basis of the variation of the equilibrium constant with temperature Van't Hoff suggested that the logarithm of the rate constant of a reaction should bear an inverse relationship to the absolute temperature. Arrhenius applied this idea to a number of reactions and showed that:

$$\ln k = \ln A - \frac{E}{RT}$$

where T is the absolute temperature, R the gas constant and A and E are constants characteristic of the reaction and now called the A factor and the activation energy, respectively. He suggested that an equilibrium existed between inert and active molecules and that only the latter could react.

According to a simple form of the Maxwell-Boltzmann Distribution Law the fraction of molecules in a gas having energy greater than E is: *in 2 degrees of freedom*

$$\frac{n_e}{n_0} = e^{-E/RT}$$

The Arrhenius equation written in the form:

$$k = Ae^{-E/RT}$$

bears a striking resemblance and suggests the interpretation that only those molecules with energy in excess of a minimum amount, E , are capable of reacting.

Calculation of Activation Energies: London¹⁷ showed that it might be possible to calculate the activation energy of a reaction using the methods of quantum mechanics. He pointed out that many reactions are adiabatic in the

sense that they do not involve electronic transitions; for such reactions it is possible to represent the state of an electron by a single function throughout the course of the reaction and London derived an approximate expression for the potential energy (P.E.) of a system of three atoms X, Y and Z, each having one uncoupled s electron:

$$\text{P.E.} = A + B + C + \left\{ \frac{1}{2} [(\alpha-\beta)^2 + (\beta-\gamma)^2 + (\gamma-\alpha)^2] \right\}^{\frac{1}{2}} \quad \text{I.1}$$

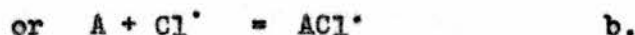
where A, B and C are the coulombic interactions of the electrons on X and Y, Y and Z and Z and X, respectively, and α , β and γ are the corresponding resonance or exchange energies. The values of A, B, C, α , β and γ depend on the interatomic distances and it is thus possible to calculate a potential energy surface giving the variation of potential energy for all possible interatomic distances by solving the appropriate integrals.

The reaction $XY + Z = X + YZ$ must follow a path on this surface and it may be assumed that it will follow the easiest path. For a system of three atoms it can be shown that a linear configuration requires the minimum energy for a reaction involving three s electrons and it is, therefore, only necessary to consider one potential energy surface.

The exact solution of the integrals from which the separate coulombic and resonance energies can be obtained is extremely difficult even for the simplest possible case of two hydrogen atoms. An approximate solution was suggested by Eyring and Polanyi¹⁸ for the system: $\text{H}^{\bullet} + \text{H}_2\text{p} = \text{H}_2\text{o} + \text{H}^{\bullet}$ using what has become known as the semi-empirical method: the total binding energy, $(A + \alpha)$ of a pair of atoms X and Y and its variation with distance can be derived from spectroscopic data and expressed in terms of the Morse equation²⁹ and, by assuming that the coulombic energy is a constant fraction of the total,

a potential energy surface can be constructed by using equation I.1 and the activation energy for the reaction evaluated.

For more complicated reactions such as:



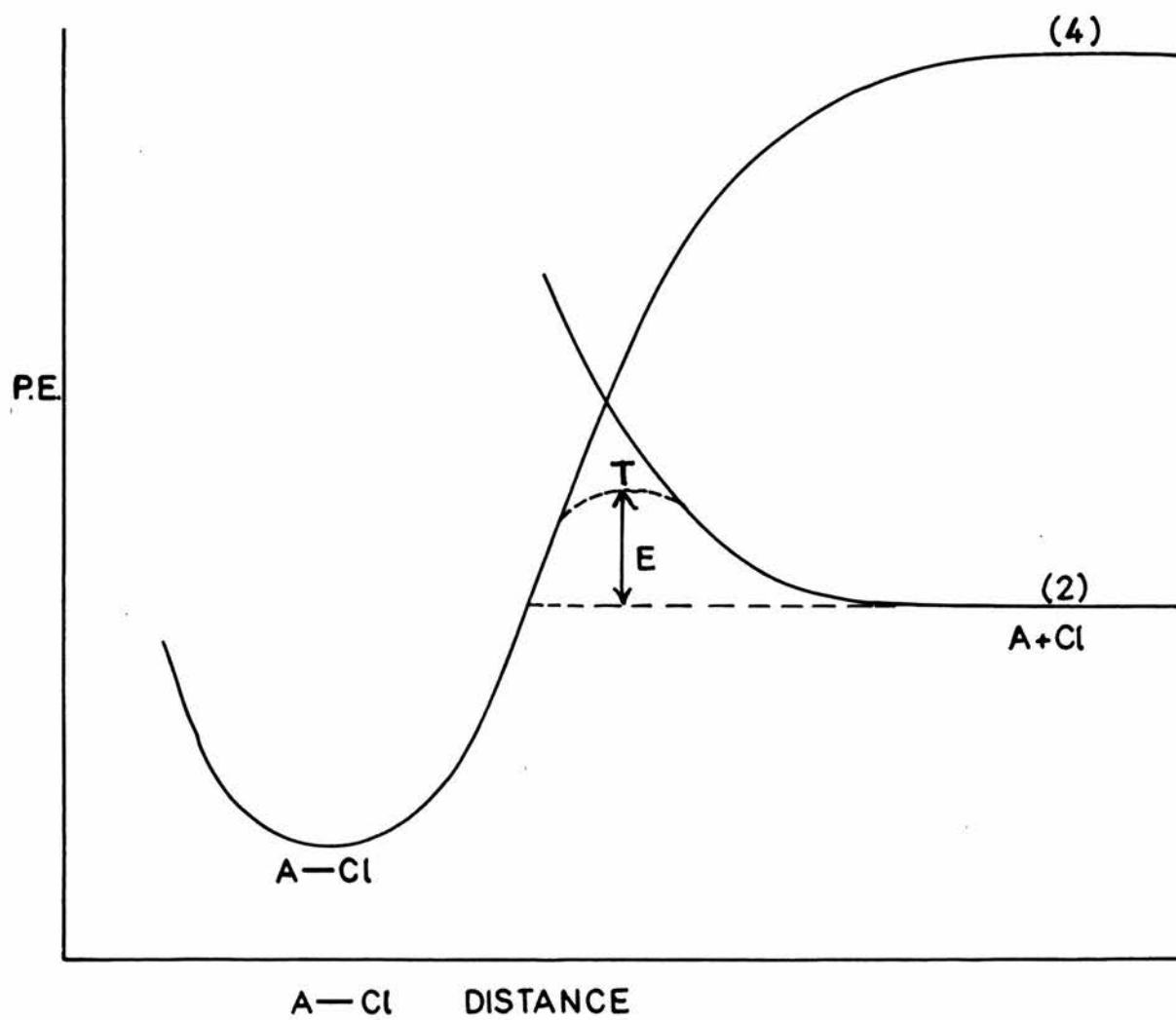
the calculations are even more difficult but generally the activation energy depends on the following five factors:

1. The strength of the bond broken (R-H)
2. The repulsion energy between Cl[•] and RH or A
3. The repulsion energy between R[•] and HCl
4. The strength of the bond formed (H-Cl, A-Cl)
5. Resonance in the activated complex.

Positive increments in 1-3 should increase the activation energy for the reaction whereas an increase in 4 and 5 should decrease it. Reaction b. is only affected by factors 2, 4 and 5 and they are represented in figure I.1 - the simplifying assumption is made that the length of the C-C bond does not change appreciably during the reaction. The point of highest energy (T) corresponds to the "transition state" or "activated complex" and the difference between this energy and that of the reactants is the activation energy, E.

The Collision Theory: The exponential term in the Arrhenius equation may be regarded as that fraction of the total number of molecules that possesses the necessary energy to enable them to react. In 1918 Lewis³⁰ suggested that A is equal to the frequency of collision between reactant molecules, at least for bimolecular gas phase reactions. The standard collision frequency, Z, between two species A and B is given by:

FIG. I.1



$Z = \sigma_{AB}^2 \left[8\pi K T \frac{m_A + m_B}{m_A m_B} \right]^{\frac{1}{2}}$ molecules⁻¹ cc.sec.⁻¹ where σ_{AB} is the mean collision diameter of A and B, K is Boltzmann's constant, T is the absolute temperature and m_A and m_B are the masses of A and B.

The relationship $k = Z e^{-E/RT}$ was found to hold for some gas reactions but frequently the experimental value of k was much lower than the calculated value and it was suggested that, for more complex molecules, a critical orientation of the molecules on collision might be necessary for reaction to occur and a steric factor, P, was introduced: $k = PZ e^{-E/RT}$.

This could not explain, however, the fact that k was occasionally higher than the calculated value. Furthermore, the equilibrium constant, K, for a reaction may be written:-

$$K = \frac{k_1}{k_2} = \frac{P_1 Z_1 e^{-E_1/RT}}{P_2 Z_2 e^{-E_2/RT}}$$

where the subscripts 1 and 2 refer to the forward and reverse reactions, respectively.

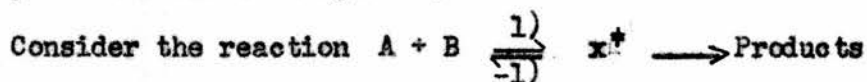
$$\therefore K = \frac{P_1 Z_1}{P_2 Z_2} e^{-(E_1 - E_2)/RT} = \frac{P_1 Z_1}{P_2 Z_2} e^{-\Delta H/RT}$$

But, from thermodynamics, $K = e^{-\Delta G/RT}$ and it follows that $\frac{P_1 Z_1}{P_2 Z_2} = e^{\Delta S/R}$.

It would, therefore, be expected that PZ would involve an entropy of activation and the collision theory provides no means of evaluating P.

Absolute Theory of Reaction Rates¹⁹: It has been shown that a reaction may be regarded as proceeding via an activated complex and for the statistical treatment of rates it is assumed that the initial reactants are always in equilibrium with the activated complex and that the latter decomposes at a definite rate.

The activated state is imagined to exist at the top of the energy barrier in a potential box of length δ .



the equilibrium constant, $K^\ddagger = \frac{k_1}{k_{-1}} = \frac{c^*}{c_A \cdot c_B} = \frac{Q_1^*}{Q_A \cdot Q_B} e^{-E_0/RT}$ I.2

where the c 's are concentrations (ideal behaviour assumed) and the Q 's the partition functions per unit volume of the species A, B and x^* and E_0 is the energy increase at absolute zero when one mole of the activated complex is formed.

Also, the rate of reaction, $R_{Pr} = k_1) c_A \cdot c_B = \frac{c^*}{2} \left(\frac{2KT}{\pi m^*} \right)^{\frac{1}{2}} \frac{1}{\delta}$ I.3

since half of the activated complexes will be moving in one direction across the barrier with a mean velocity, $\bar{v} = \left(\frac{2KT}{\pi m^*} \right)^{\frac{1}{2}}$ and the length of barrier = δ .

From I.2 and I.3 $k_1) = \frac{c^*}{c_A c_B} \left(\frac{KT}{2\pi m^*} \right)^{\frac{1}{2}} \frac{1}{\delta} = \frac{Q_1^*}{Q_A \cdot Q_B} \left(\frac{KT}{2\pi m^*} \right)^{\frac{1}{2}} \frac{1}{\delta} e^{-E_0/RT}$ I.4

Replacing Q_1^* by $Q_+ \cdot \frac{(2\pi m^* KT)^{\frac{1}{2}} \delta}{h}$, where $\frac{(2\pi m^* KT)^{\frac{1}{2}} \delta}{h}$ is the translation partition coefficient in the reaction co-ordinate, we have

$$k_1) = \frac{KT}{h} \frac{Q_+}{Q_A Q_B} e^{-E_0/RT} \quad \text{I.5}$$

$$= \frac{KT}{h} K^\ddagger \quad \text{I.6}$$

From thermodynamics $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$

$$\text{and } -\Delta G^\ddagger = RT \ln K^\ddagger$$

$$\therefore k_1) = \frac{KT}{h} e^{-\Delta H^\ddagger/RT} e^{\Delta S^\ddagger/R} \quad \text{I.7}$$

From I.6 $\frac{d \ln k_1)}{dT} = \frac{1}{T} + \frac{d \ln K^\ddagger}{dT}$ I.8

and from the Arrhenius equation $\frac{d \ln k_1}{dt} = \frac{E_{exp}}{RT^2}$ I.9

$$\therefore \frac{E_{exp}}{RT^2} = \frac{1}{T} + \frac{\Delta U^\ddagger}{RT^2} \quad I.10$$

since K^\ddagger is a concentration equilibrium constant.

$$\therefore E_{exp} = RT + \Delta U^\ddagger = RT + \Delta H^\ddagger - P \cdot \Delta V^\ddagger$$

where ΔU^\ddagger = increase in internal energy for the activation process,

ΔH^\ddagger = heat of activation

and ΔV^\ddagger = accompanying increase in volume at constant pressure, P.

But $P \cdot \Delta V^\ddagger = \Delta n^\ddagger RT = -RT$ for a bimolecular gas reaction.

$$\therefore \text{from I.7 } k_1) = \frac{KT}{h} e^{2e} e^{\Delta S_c^\ddagger/R} e^{-E_{exp}/RT} \quad I.11$$

Thus, for a bimolecular reaction which proceeds via an activated complex, the theory of absolute reaction rates predicts that the experimental A factor =

$$\frac{KT}{h} e^{2e} e^{\Delta S_c^\ddagger/R}$$

where ΔS_c^\ddagger is the entropy of activation at constant concentration and can be calculated if the entropies of the complex and the reactants are known.

$$\Delta S_c^\ddagger = \Delta S_{trans}^\ddagger + \Delta S_{vib}^\ddagger + \Delta S_{rot}^\ddagger$$

Since ΔS_c^\ddagger is temperature dependent the A factor should be calculated for the middle of the temperature range.

It will be noted that, as suggested in the last section, A involves an entropy of activation. For a reaction between two atoms equation I.5 becomes

$$k_1) = \frac{KT}{h} \left[\frac{2\pi(m_A + m_B)KT}{h^3} \right]^{3/2} \frac{8\pi KT}{h^2} \frac{m_A m_B}{m_A + m_B} d_{AB}^2 e^{-E_c/RT}$$

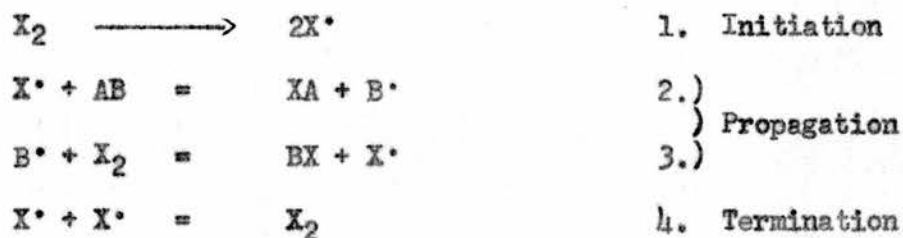
$$\frac{(2\pi m_A KT)^{3/2}}{h^3} \cdot \frac{(2\pi m_B KT)^{3/2}}{h^3}$$

and this reduces to $k_1) = d_{AB}^2 \cdot 8 \pi K T \left(\frac{m_A + m_B}{m_A m_B} \right) e^{-E_0/RT}$

Provided that d_{AB} , the distance between the nuclei in the activated complex, is identified with the collision diameter this is equivalent to the expression derived earlier on the basis of the kinetic theory which is therefore valid for reacting species having no rotational or vibrational degrees of freedom. The steric factor thus appears to be related to the loss of rotational and the gain of vibrational motion or entropy when more complex species react. For example, for Cl^+ + polyatomic molecule there is a net loss compared to Cl^+ + atom of two degrees of rotational motion and a net gain of two degrees of vibrational motion. Since $Q_{vib} \sim 0.1-0.2 Q_{rot}$, it might be expected that the steric factor would be between 0.1 and 0.01 for such reactions. This is in general borne out by experiment.

3. Determination of Rate Constants and Arrhenius Parameters of Elementary Reactions

To test the validity of the theories just outlined it is necessary to compare calculated Arrhenius parameters with those obtained from experiment. Gas phase atom and free radical reactions are important because they are inherently simple and approximate calculations of their Arrhenius parameters may be possible. However, their experimental evaluation is complicated by the fact that elementary radical reactions are often part of a chain mechanism and the concentration of radicals is extremely low and therefore difficult to measure directly and the determination of rate constants for the individual elementary reactions then depends on an analysis of a complex rate constant in the light of an assumed reaction mechanism. Consider the chain reaction



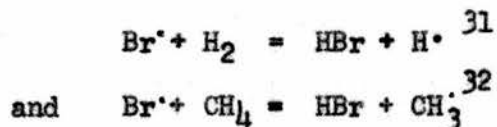
The rate of 2. is given by $R = k_2 [AB][X^\bullet]$

To determine the specific rate constant, k_2 , it is necessary to know a) the concentration of AB, b) the rate of removal of AB or production of XA and c) the concentration of X^\bullet . a) and b) can usually be obtained quite easily; c) cannot in general be determined directly. One exception is the reaction $Cl^\bullet + H_2 = HCl + H^\bullet$ studied by Rodebush and Klingelhoeffer¹⁰ who generated chlorine atoms in an electrodeless discharge and measured their concentration with a Wrede-Harteck diffusion gauge.

Applying the steady state approximation, the overall rate of the above reaction is given by

$$R = k_2 [AB][X^\bullet] = k_2 [AB] \left(\frac{2k_1 [X_2]}{k_4} \right)^{\frac{1}{2}} = K^{\frac{1}{2}} k_2 [AB] [X_2]^{\frac{1}{2}}$$

Where K , the equilibrium constant for the dissociation of X_2 is known, k_2 can be calculated if R , $[AB]$ and $[X_2]$ can be measured. This approach was used to obtain values for the rate constants of the reactions



(In both cases allowance had to be made for the rate of the reverse reactions, -3).

The activation energy for the overall reaction is $(E_2 + \frac{1}{2}D(X_2) - E_4)$ where $D(X_2)$ is the heat of dissociation of the dimer so that the overall activation energy is usually large and the temperature range over which experiments can be carried out limited.

The temperature range can be extended by carrying out photochemical experiments in which case the overall activation energy is $(E_2 - \frac{E_4}{2})$ and, if E_4 is assumed to be zero, E_2 can be obtained. The A factor cannot, however, be obtained by the photochemical method and it is necessary to determine the absolute rate constant at at least one temperature by the thermal method. Benson and Buss³³ have investigated the conditions under which the thermodynamic concentration of atoms is established and show that, for certain bromine atom reactions and for chlorine atom reactions where the chains are exceedingly long and there are other chain terminating processes, a considerable amount of reaction occurs in the prestationary state period and the steady state approximation cannot be applied. In photochemical experiments the induction period is shorter and meaningful activation energies can be obtained but, as pointed out above, it is not possible to obtain A factors by this method.

Another problem in determining individual rate constants from a study of the overall kinetics of a reaction is that the complex rate constant depends on the chain ending step. Thus, if reaction 4 is replaced by



the rate equation becomes

$$R = \left\{ \frac{2k_1 k_2 k_3}{k_5} [AB] [X_2]^2 \right\}^{\frac{1}{2}} \quad \text{and}$$

$$R = \left(\frac{2k_1}{k_6} \right)^{\frac{1}{2}} [X_2]^{3/2}, \text{ respectively.}$$

Furthermore, more than one chain terminating step may occur at the same time and their relative importance can change during the course of a reaction, if the ratio of $[AB] : [X_2]$ changes.

The mean lifetime, τ_s , of a radical under stationary state conditions is given by

$$\tau_s = \frac{\text{Stationary State concentration of radicals}}{\text{Rate of removal of radicals}}$$

If termination is entirely by 4. $\tau_s = \frac{[X^{\cdot}]}{k_4 [X^{\cdot}]^2} = \frac{1}{k_4 [X^{\cdot}]}$

In photochemical experiments $k_4 [X^{\cdot}]^2 = 2 I_{abs}$

$$\therefore \tau_s = \frac{1}{(2k_4 I_{abs})^{\frac{1}{2}}}$$

I_{abs} is readily obtained and, if τ_s can be measured, k_4 and hence k_2 can be calculated since $R = k_2 \left(\frac{2I_{abs}}{k_4} \right)^{\frac{1}{2}} [AB]$.

Radical lifetimes can be measured experimentally by the rotating sector technique²² and this method has been used to evaluate the rate constants of a number of elementary reactions occurring in photochlorinations²⁸. As with

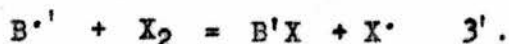
the direct methods the rate constant obtained depends on the radicals involved in termination. Furthermore, the method can only be applied to systems for which n , the exponent of I_{AB} , is less than one. In chlorinations the chains are long and the rate is sensitive to the presence of inhibitors: extreme purity of reactants is therefore essential.

The disadvantages inherent in the methods discussed above can be avoided by using a competitive technique. Thus, if reaction 2. is allowed to compete with 2'



$$\frac{R_2'}{R_2} = \frac{k_2' [X \cdot] [AB']}{k_2 [X \cdot] [AB]} = \frac{k_2' [AB']}{k_2 [AB]} = \frac{-d[AB'] / dt}{-d[AB] / dt}$$

and, if the chains are long and 2' is followed by 3'



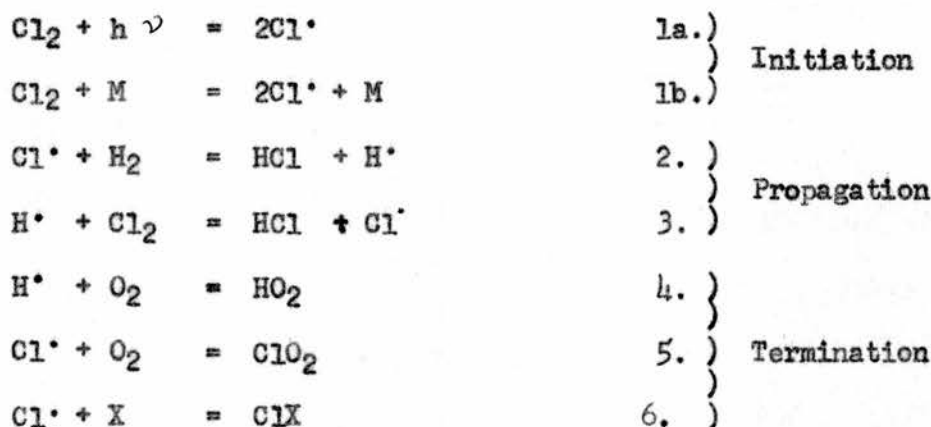
$$\frac{R_2'}{R_2} = \frac{+d[B'X] / dt}{+d[BX] / dt}$$

Therefore, if k_2' is known, k_2 can be determined by measuring the relative rates of consumption of reactants or appearance of products. The free radical concentration does not enter into the expression for k_2' / k_2 : thus the nature and rate of the initiation and termination processes are unimportant provided the chains are long; it is not necessary that the stationary state be established and extreme purity of reactants is not essential. Another feature of this method is that it is always k_2 that is obtained.

The reaction $Cl \cdot + H_2 = HCl + H$ has been used as the absolute standard in competitive chlorination studies³⁴ and the value of the rate constant for this reaction will be considered in the following section. The applicability of the competitive method to the propane/olefine system will be discussed after the chlorination of hydrocarbon derivatives has been reviewed.

4. The Reaction of Chlorine with Hydrogen

The hydrogen/chlorine system has been the subject of many investigations; much of the data is contradictory and Benson³⁵ suggests that this is because the chain system (H_2+Cl_2) cannot reach a stationary state as the chain cycle is too fast relative to chain termination. The reaction mechanism has been considered in detail elsewhere^{31, 36}, and only the main conclusions will be outlined here. The following mechanism, originally suggested by Gohring³⁷ is now generally accepted.



The nature of X is uncertain but there is some evidence that it is a compound of silicon³⁸. Applying the steady state approximation

$$\frac{d[HC1]}{dt} = \frac{(2 Iabs) k_2 k_3 [H_2] [Cl_2]}{k_3 k_6 [Cl_2] [X] + k_3 k_4 [O_2] ([H_2] + k_3 k_5 [Cl_2])}$$

if the terms $k_4 k_5 [H] [O_2]^2$ and $k_4 k_6 [X]$ are neglected and this agrees with the experimental law of Bodenstein and Unger³⁸:

$$\frac{d[HC1]}{dt} = \frac{k Iabs [H_2] [Cl_2]}{m [Cl_2] + [O_2] \left([H_2] + \frac{[Cl_2]}{10} \right)}$$

At low pressures of oxygen the above equation reduces to

$$\frac{d [\text{HCl}]}{dt} = \frac{2 I_{\text{abs}} [k_2] [\text{H}_2]}{k_6 [\text{X}]}$$

which is in agreement with the experimental rate law^{38,39}.

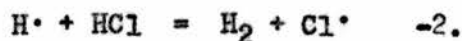
From the temperature coefficient of the reaction, and assuming $E_6=0$, Hertel⁴⁰ obtained $E_2 = 5.9 \pm 0.5$ k cal. mole⁻¹ at room temperature while Potts and Rollefson³⁹ found $E_2 = 5.8$ kcal. mole⁻¹ above 200°K and $E_2 = 4.6$ k cal. mole⁻¹ below 170°K.

The currently accepted value for the Arrhenius parameters of the reaction $\text{Cl} \cdot + \text{H}_2 = \text{HCl} + \text{H} \cdot$ 2. depends on three independent sets of experiments carried out at widely different temperatures. Rodebush and Klingelhoeffer¹⁰ generated chlorine atoms in an electrodeless discharge and measured their concentration directly with a Wrede-Hartek diffusion gauge. The chlorine atoms were allowed to react with hydrogen in a flow system and the probability, W , of a chlorine atom reacting with a hydrogen molecule found .

$$W = \frac{\text{HCl formed}}{\text{Cl} \cdot \text{ introduced}} / 2Z'$$

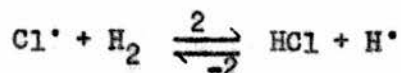
where Z' is the average number of collisions between a given chlorine atom and a hydrogen molecule in the reaction vessel as calculated from kinetic theory. The authors used the relationship $W \propto \frac{(1+E_2)}{(RT)} e^{-E_2/RT}$ and obtained from the temperature dependence of W over 273-298°K a value of $E_2 = 6,100 \pm 1000$ cal. mole⁻¹. The relationship $W \propto e^{-E_2/RT}$ gives $E_2 = 5,550$ cal. mole⁻¹.

Steiner and Rideal⁴¹ obtained the rate constant for the reaction



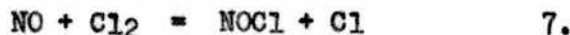
by studying the hydrogen chloride catalysed conversion of ortho-to-para-hydrogen in the temperature range 900-1070°K. Combining those values with

the known equilibrium constant for

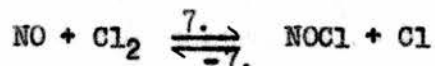


they calculated k_2 and obtained an energy of activation, E_2 , of 5,900 cal. mole⁻¹.

Ashmore and Chammugam⁴² obtained a value of k_2 at 523°K by studying the chlorination of hydrogen in the presence of NOCl and NO. At this temperature the most important initiating reaction is

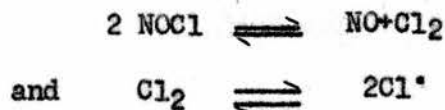


and they were able to show that the concentration of chlorine atoms is very close to the thermodynamic equilibrium concentration for the system



and that $\frac{d[\text{HCl}]}{dt} = \alpha [\text{H}_2] [\text{Cl}_2] \frac{[\text{NO}]}{[\text{NOCl}]}$ where $\alpha = (1.85 \pm 0.15) \frac{k_2 k_7}{k_{-7}}$

k_7/k_{-7} was calculated from the known equilibrium constants for the reactions



and k_2 thus evaluated. In this system slow attainment of the stationary state does not arise since the activation energies for both 7. and -7. are low.

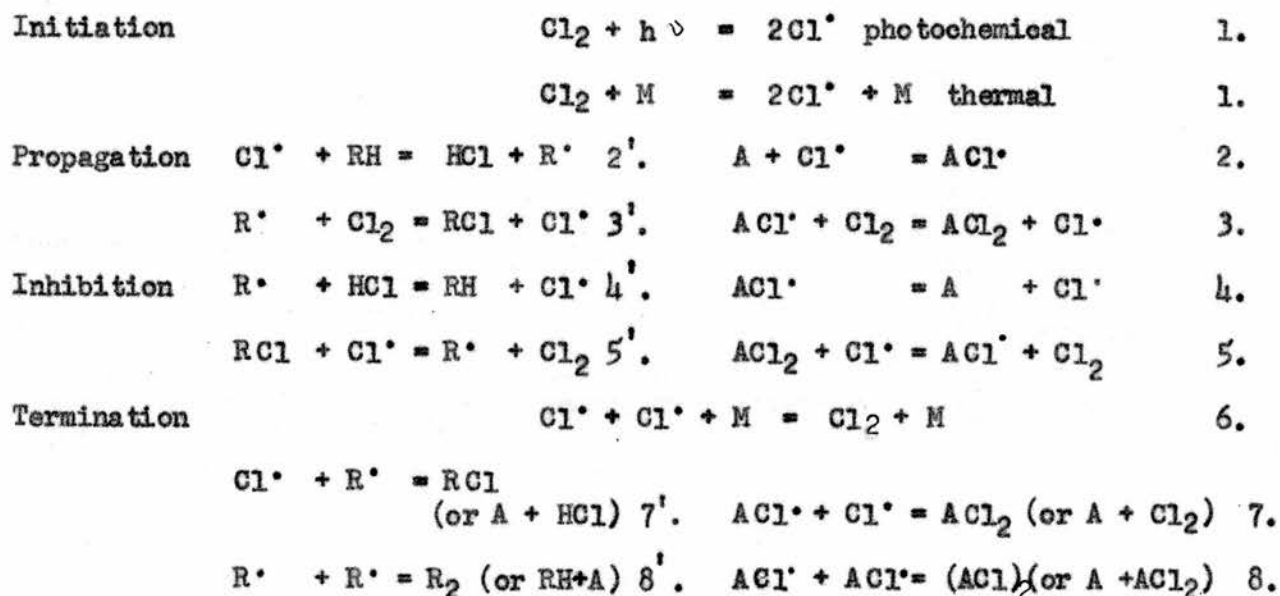
A least squares treatment of the combined results gave

$k_2 = 0.8 \times 10^{11} \exp. (-5,500 \pm 200 / RT) \text{ l.mole}^{-1} \cdot \text{sec}^{-1}$. Fettes and Knox³⁴ have recently recalculated Steiner and Rideal's results using modern thermodynamic data and obtain from the three sets of results

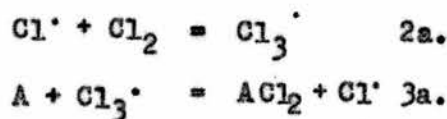
$$k_2 = (8.3 \pm 0.6) 10^{10} \exp. (-5,480 \pm 140 / RT) \text{ l.mole}^{-1} \cdot \text{sec}^{-1}.$$

5. Chlorination of Hydrocarbon Derivatives.

This subject has recently been considered in reviews by Chiltz et.al.²⁸ and by Fettis and Knox³⁴. The following general mechanism is used where RH = saturated hydrocarbon and A= olefine.



It may be noted that the Rollefson mechanism for the photochlorination of olefines replaces 2. and 3. by



; termination is by 6. and the rate law becomes $R = \left(\frac{2I_{abs}}{k_6} \right)^{\frac{1}{2}} k_{2a} Cl_2$. Rate laws of this form are obtained but the rates are not the same for different A's as predicted by this equation and the mechanism can be discarded.

5 and 5' do not occur at low temperatures since they involve activation energies of $\sim 20 \text{ kcal.mole}^{-1}$ whereas the activation energy for the competing reaction 2 is less than 5 kcal.mole^{-1} ²⁸. Similarly 4' is unlikely to be important as $E_{4'} - E_{3'}$ is usually large compared with $E_{3'}$ ²⁸ and there is

little evidence of inhibition by HCl although Newton and Rollefson found that some CDCl_3 was formed when CHCl_3 was chlorinated in the presence of DCl^{43} . k_4 is unimolecular and in principle about 10^5 times as fast as the corresponding bimolecular reaction of the same activation energy at a pressure of about 100 mm Hg. The addition of a chlorine atom to a double bond proceeds with nearly zero activation energy so that the activation energy (E_4) for the dissociation reaction is approximately equal to the dissociation energy, $D(\text{A}-\text{Cl})$. In the series $\text{A} = \text{C}_2\text{H}_m\text{Cl}_{m-4}$, $m = 0-4$, $D(\text{A}-\text{Cl})$ has a minimum value of $16.8 \text{ kcal.mole}^{-1}$ and k_4 should not, therefore, be important below $\sim 420^\circ\text{K}^{44}$ - the change in mechanism at higher temperatures has in fact been observed⁴⁵. Dainton and co-workers have suggested that the radical ACl^\bullet is formed in a vibrationally excited state and can decompose spontaneously⁴⁶: this point will be discussed later.

Applying the steady state approximation

$$\frac{d[\text{RCl}]}{dt} = \frac{(2 I_{\text{abs}})^{\frac{1}{2}} k_3 [\text{Cl}_2]}{(k_6 [\text{M}] \alpha^2 + k_7 \alpha + k_8)^{\frac{1}{2}}} \quad \text{where } \alpha = \frac{k_3 [\text{Cl}_2]}{k_2 [\text{RH}]} = \frac{[\text{Cl}^\bullet]}{[\text{R}^\bullet]} \quad \text{I.12}$$

For the thermal reaction $(2 I_{\text{abs}})^{\frac{1}{2}}$ must be replaced by $(2k_1 [\text{Cl}_2])^{\frac{1}{2}}$ and similar expressions hold for the chlorination of saturated hydrocarbons.

The predominating termination reaction depends on the relative values of k_6 , k_7 and k_8 and on the ratio $\frac{k_3 [\text{Cl}_2]}{k_2 [\text{RH}]}$. Reaction 6 is termolecular and is only important at low olefine and high chlorine pressures. Under those conditions linear removal of chlorine atoms also occurs. Generally 7. and 8. predominate⁴⁷ and the equation given above becomes

$$\frac{d[\text{RCl}]}{dt} = \frac{(2 I_{\text{abs}})^{\frac{1}{2}} k_3 [\text{Cl}_2]}{(k_7 k_3 [\text{Cl}_2] / k_2 [\text{RH}] + k_8)^{\frac{1}{2}}}$$

Obviously the relative importance of 7 and 8. will depend on the ratio $[Cl_2]/[RH]$ and may, therefore, change during the course of the reaction.

Thus the determination of rate constants from a study of the overall kinetics of the reaction or by means of the rotating sector technique is complicated and usually gives k_3 , although Dainton⁶³ used the latter method to obtain k_2 for ¹³Cis dichloroethylene by working at high chlorine and low olefine pressures. For determining k_2 , however, the competitive method is generally more useful. By combining the results of Knox⁴⁸ on the competitive chlorination of the chloromethanes against propane with those of Knox and Nelson⁴⁹ on the competitive chlorination of unsubstituted hydrocarbons two closed circuits were obtained in which every adjacent pair had been chlorinated in competition:

- (i) methane, ethane, propane, methylene chloride, methane.
- (ii) methane, ethane, propane, methylehloride, chloroform, methane.

The internal consistency of the results was good. The competitive chlorinations of the chloromethanes and pentoehloroethane against tetrachloroethylene have been studied by Goldfinger and co-workers⁵⁰ and of ethylene, propylene and isobutene against propane by Hagopian and Knox^{51,52}. Using the Arrhenius parameters for $Cl\dot{+}CH_4 = HCl + CH_3\dot{}$, obtained from the competitive chlorination of methane and hydrogen and the known result for $H_2 + Cl\dot{=} HCl + Cl\dot{}$, Knox and co-workers calculated the corresponding values for the compounds listed above and Goldfinger et al. used Knox's results for the chloromethanes to calculate Arrhenius parameters for the reactions of $Cl\dot{}$ with tetrachloroethylene and pentoehloroethane.

Evidence for the mechanism of olefine chlorination and for the rate constants of the elementary reactions involved will be discussed after the chlorination of propane, the competitive standard in this work, has been considered.

5(a) Chlorination of Propane

Yuster and Reyerson⁵³ chlorinated propane in a flow system and concluded that it was a free radical chain reaction with very long chains. They suggested that the initial irreproducibility of the results was due to surface initiation and termination processes and that the surface was poisoned by the chlorinated products. Further evidence for a free radical mechanism was obtained by Vaughan and Rust⁵⁴ who showed that the thermal chlorination of propane was initiated by tetraethyl lead.

Hass, McBee and Weber⁵⁵ chlorinated propane thermally between 50° and 600°C in a large scale flow system and separated the products by fractional distillation. They showed that chlorine atom attack at a secondary carbon-hydrogen bond was faster than at a primary bond and that the relative rates of attack approached unity as the temperature increased. Steiner and Watson⁵⁶ used their results to obtain a value for (E_2' prim - E_2' sec.) of 1.35 kcal. mole⁻¹. However, the Arrhenius plots curved badly and gave unreliable results due to polysubstitution and pyrolysis of products at higher temperatures.

Pritchard, Pyke and Trotman-Dickinson⁵⁷ studied the competitive chlorination of the following pairs of compounds - $H_2:CH_4$, $CH_4:C_2H_6$, $C_2H_6:C_3H_8$. They followed the reaction by observing the rate of disappearance of reactants and were thus unable to obtain relative rates of attack at different positions in the same molecule. For the overall chlorination of propane they obtained (E_2' ethane - E_2' propane) = 330±200 cal.mole⁻¹ and, by utilising the known parameters for $H_2+Cl\cdot \rightarrow HCl+H\cdot$, they calculated k_2' propane = $1.76 \times 10^{11} e^{-670/RT}$ l.mole⁻¹ sec.⁻¹.

The use of gas chromatography enabled Knox²⁰ to analyse the products of the photochlorination of propane and he found

$$k_2'_{iso} / k_2'_{n-} = 0.55 \exp. (+445 \pm 30/RT)$$

Product analyses by gas chromatography was also used to study the competitive chlorinations of hydrogen/methane⁴⁹, methane/ethane²⁶ and ethane/propane⁴⁹ mixtures and, by combining the results from those experiments with the value

$$k_2'(Cl+H_2) = (8.3 \pm 0.6) 10^{10} \exp. (-58404/RT) \text{ l.mole}^{-1} \text{ sec}^{-1}$$

recently recalculated by Fettis and Knox³⁴, the Arrhenius parameters for the attack of a chlorine atom on the primary and secondary C-H bonds in propane were calculated. The results are quoted in the accompanying table and the value for the attack of a chlorine atom at the primary position have been used as the standard in this work.

	$10^{-10} A \text{ l.mole}^{-1} \text{ sec}^{-1}$ per H atom	E cal.mole ⁻¹
Primary C-H Bond	1.7 ± 0.3	980 ± 130
Secondary C-H Bond	3.6 ± 0.7	660 ± 130

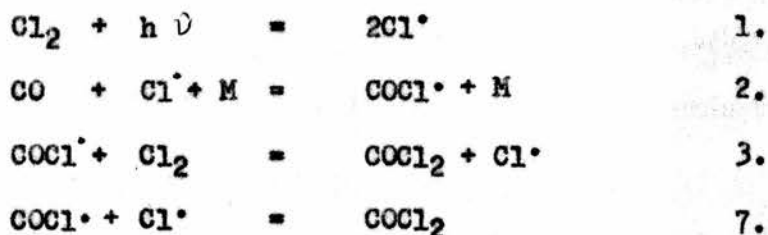
5(b) Chlorination of Carbon Monoxide

The photochemical formation of phosgene from carbon monoxide and chlorine has been the subject of many investigations³¹ and will be considered briefly since the mechanism of the reaction is similar to that for the chlorination of olefines.

The bulk of the early work was carried out in the laboratories of Rollefson and of Bodenstein and both obtained the empirical rate law -

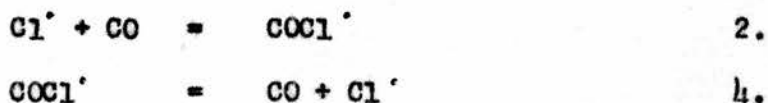
$$\frac{d [COCl_2]}{dt} = k(I_a)^{\frac{1}{2}} [Cl_2] [CO]^{\frac{1}{2}}$$

Their interpretation of the mechanism was, however, different. Lenher and Rollefson⁵⁸ suggested the following reaction scheme:



Provided $\text{M} = \text{Cl}_2$ this scheme gives the observed rate law where $k = \left(\frac{k_2 k_3}{k_7}\right)^{\frac{1}{2}}$

The mechanism assumed by Bodenstein, Brenschede and Schumacher⁵⁹ replaced reaction 2. of the above scheme by



By assuming that $k_4 \gg k_3 [\text{Cl}_2]$, which means that an equilibrium $\text{COCl}^\bullet \xrightleftharpoons{4} \text{CO} + \text{Cl}^\bullet$ is established, and the usual condition for long chains ($k_7 [\text{Cl}_2] \ll k_3 [\text{Cl}_2]$) it can be shown that

$$\frac{d[\text{COCl}_2]}{dt} = \frac{k_3 (2 I_{\text{abs}})^{\frac{1}{2}} [\text{Cl}_2] [\text{CO}]^{\frac{1}{2}}}{(k_7 K_{\text{COCl}^\bullet})^{\frac{1}{2}}} \quad \text{where } K = \frac{[\text{CO}][\text{Cl}^\bullet]}{[\text{COCl}^\bullet]} = \frac{k_4}{k_2}$$

The system was carefully reinvestigated by Burns and Dainton⁶⁰ who obtained the same rate law and provided further evidence for the Bodenstein mechanism. They used the rotating sector technique to evaluate the lifetime of the radical chains under different conditions and from their results calculated the following constants:

$$\begin{array}{l}
 k_3 = 10^{9.4} \exp. (-2960/RT) \text{ l.mole}^{-1} \text{ sec}^{-1} \\
 k_7 = 10^{11.6} \exp. (-830/RT) \text{ l.mole}^{-1} \text{ sec}^{-1} \\
 K_{\text{COCl}^\bullet} = 10^{2.806} \exp. (-6,310/RT) \text{ mole l}^{-1}
 \end{array}$$

It follows that $E_4 \leq 6.3 \text{ kcal.mole}^{-1}$ in contrast with the expected value of $E_4 > 16 \text{ kcal.mole}^{-1}$ for ethylene and the chloroethylenes²⁸ and, for the reaction between carbon monoxide and chlorine, $k_4 \gg k_3 [\text{Cl}_2]$ and the equilibrium $\text{COCl}' \rightleftharpoons \text{CO} + \text{Cl}'$ can be established. Assuming $k_4 = 100 k_3 [\text{Cl}_2]$ at 25°C in the presence of 100 mm Cl_2 , $A_4 = 10^{11.6} \text{ sec}^{-1}$ which is of the order expected for the unimolecular decomposition of a weak link.

5 (c) Chlorination of Olefines:

Dichloroethylene: The photochlorination of trans dichloroethylene was investigated by Müller and Schumacher⁶¹ who found it to be a chain reaction with a quantum yield of about 7×10^3 moles einstein⁻¹. The rate of formation of tetrachloroethane was given by

$$\frac{d [\text{C}_2\text{H}_2\text{Cl}_4]}{dt} = k I_a^{\frac{1}{2}} [\text{Cl}_2]$$

The reaction was strongly inhibited by oxygen and had an overall activation energy of $3.1 \text{ kcal.mole}^{-1}$. The same workers found that the photochlorination of cis dichloroethylene was similar and in fact proceeded with the same absolute rate. They proposed a mechanism involving reactions 1, 2, 3 and 8 of the general scheme given above from which it can be shown that $k = \left(\frac{2}{k_8}\right)^{\frac{1}{2}} k_3$

It would be expected that E_4 would have a value close to the bond dissociation energy, $D (\text{C}_2\text{H}_2\text{Cl}_2 - \text{Cl}) = 20.3 \text{ kcal.mole}^{-1}$ ²⁸, and that the decomposition of the radical would compete increasingly with its reaction with chlorine as the temperature increases, and when reaction 4. ceases to be negligible the rate expression should become

$$\frac{d [\text{C}_2\text{H}_2\text{Cl}_4]}{dt} = \frac{k_3 [\text{Cl}_2] \left\{ 2I_{\text{abs}} k_2 [\text{A}] \right\}^{\frac{1}{2}}}{\left\{ k_7 (k_3 [\text{Cl}_2] + k_4) \right\}^{\frac{1}{2}}}$$

if termination is by 7. Finally at high temperatures when $k_4 \gg k_3$ $[Cl_2]$

$$\frac{d [C_2H_2Cl_4]}{dt} = k_3 [Cl_2] \left\{ \frac{2I_{abs} k_2 [A]}{k_4 k_7} \right\}^{\frac{1}{2}}$$

Ayscough, Cocker and Dainton⁴⁶ noted that the lifetime of the radicals formed in 2. is about 10^{-5} secs. during which time there will be many rotations about the C-C bond so that, when the radical decomposes, there will be a probability x of forming trans-dichloroethylene and $(1-x)$ of forming cis-dichloroethylene. Direct evidence for 4. could therefore be obtained by comparing the rates of isomerisation of the pure isomers with their rates of chlorination and hence x and k_4/k_3 measured :

$$\frac{R_1}{R_p} = x \cdot k_4/k_3 \text{ for pure cis} = \frac{\text{trans D.C.E. formed}}{\text{tetrachloroethane formed}}$$

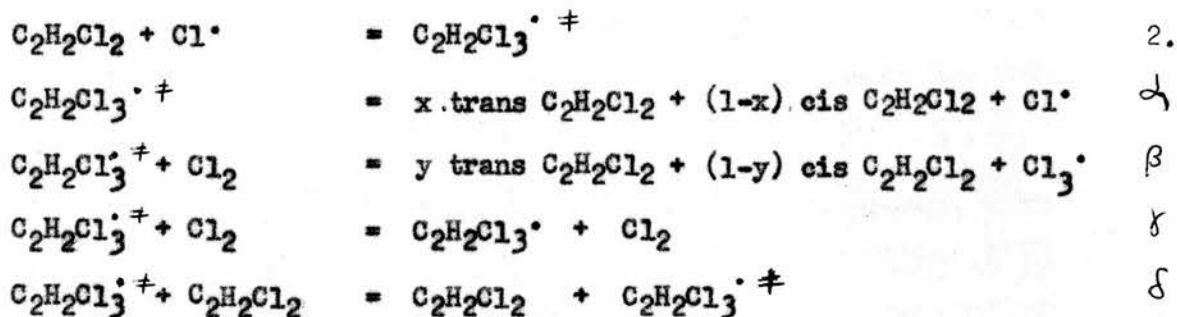
$$\frac{R_1}{R_p} = (1-x) \cdot k_4/k_3 \text{ for pure trans} = \frac{\text{cis D.C.E. formed}}{\text{tetrachloroethane formed}}$$

provided the extent of reaction is small.

It was expected that the rate of isomerisation would not be measurable below 200°C: in fact, it was appreciable at 30°C. Furthermore, R_1/R_p did not increase with temperature in accordance with the known values of E_3 and E_4 and the graphs of R_1/R_p against $[Cl_2]^{-1}$, though linear, had a positive intercept at $[Cl_2]^{-1} = 0$.

The explanation was found in the nature of the radical formed in 2: it must initially contain energy in excess of that of the same radical in its ground state by an amount $(E_2 + \Delta H_2)$. The radical was designated ACl^* since it can be regarded as the transition state of reactions 2. and 4. and

has enough energy to spontaneously decompose to the olefine and a chlorine atom (α). Alternatively, it may be collisionally deactivated (γ) or undergo atom exchange reactions with the chlorine or olefine (β , δ):



The relative rates of isomerisation and addition could then be expressed as

$$R_1/R_p = y \cdot k_\beta / k_\gamma + x \cdot k_\alpha / k_\gamma [\text{Cl}_2] \quad \text{for pure cis}$$

$$\text{and } R_1/R_p = (1-y) \cdot k_\beta / k_\gamma + (1-x) \cdot k_\alpha / k_\gamma [\text{Cl}_2] \quad \text{for pure trans}$$

and this was in accordance with the experimental behaviour. The experimental error was of the order of $\pm 10\%$ and within those limits no dependence of R_1/R_p on olefine pressure was found for pressures between 30 and 80 mm. It is perhaps surprising that the olefine apparently does not deactivate the excited radical. In this scheme reaction δ was neglected since it does not disturb the $\text{ACl}_3^\bullet \ddagger$ concentration: the fact that isomerisation would occur in this reaction was apparently neglected.

Values of x , y , k_α / k_γ and k_β / k_γ were obtained at 30, 40, 55 and 65°C and found to be virtually independent of temperature as might be expected if $\text{ACl}_3^\bullet \ddagger$ already contains the transition state energy. By assuming that every collision between an $\text{ACl}_3^\bullet \ddagger$ radical and a chlorine molecule results in either atom transfer (β) or collisional deactivation (γ), $k_\beta + k_\gamma = Z$, where Z is the rate of collision between $\text{ACl}_3^\bullet \ddagger$ and Cl_2 . Thus k_α was found to have a

value of $\sim 10^8 \text{ sec.}^{-1}$ and the lifetime of the radical ACl^\ddagger before spontaneous decomposition is, therefore, about 10^{-8} secs.

At high concentrations of olefine when termination is entirely by 8. the rate of reaction is given by

$$\frac{d[\text{ACl}_2]}{dt} = k_3 [\text{Cl}_2] \left(\frac{2I_a}{k_8} \right)^{\frac{1}{2}} \quad \text{I.13}$$

At low olefine pressures all the chlorine atoms are not removed by reaction 2. which then becomes rate determining and at very low pressures of olefine the main chain terminating step is 6. provided linear removal of atoms at the wall does not occur. Thus

$$\frac{d[\text{ACl}_2]}{dt} = \left(\frac{2I_a}{k_6M} \right)^{\frac{1}{2}} k_2 [A] \frac{k_j [\text{Cl}_2]}{k_\alpha + (k_\beta + k_j) [\text{Cl}_2]} \quad \text{I.14}$$

which reduces to

$$\frac{d[\text{ACl}_2]}{dt} = \left(\frac{2I_a}{k_6M} \right)^{\frac{1}{2}} k_2 [A] \frac{k_j}{(k_\beta + k_j)} \quad \text{I.15}$$

when $[\text{Cl}_2]$ is so high that $(k_\beta + k_j) [\text{Cl}_2] \gg k_\alpha$

The photochlorination of *cis* dichloroethylene was studied by Ayscough et al.⁶³. They showed that, at pressures of olefine greater than 16 mm., the rate of reaction was given by equation I.13 whilst at lower pressures it was dependent on olefine pressure and linearly so below 5 mm. (equation I.14). Under those conditions, however, the exponent of I_{abs} (n) was shown to be $0.5 < n < 1$ and interpreted as indicating considerable termination at the walls. By combining the results of experiments in continuous and intermittent light

at high olefine pressures values of k_3 and k_8 were obtained at 30, 40, 55 and 65°C. The resulting value of the overall activation energy (2.49±0.1) kcal.mole⁻¹ is in reasonable agreement with the value found by Müller and Schumacher.

From similar experiments at low olefine pressure the average lifetime τ , of chlorine atoms and their stationary state concentration $[Cl^\bullet] = 2 \tau I_{abs}$ were obtained and the rate constant k_2 calculated from

$$k_2 = \frac{R_p (1 + k_\beta/k_\gamma)}{2 I_{abs} \tau [A]}$$

by using the known values of k_β/k_γ . Due to the extensive linear termination k_6 could not be obtained directly from equation I.14. At a given chlorine pressure the rate of chlorination is given by

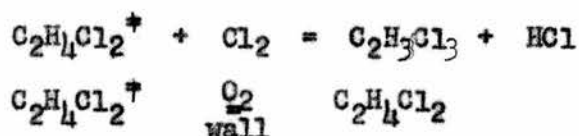
$$R_p = \frac{k_2 [A] k_\gamma [Cl_2]}{k_\alpha + (k_\beta + k_\gamma) [Cl_2]} \left\{ \frac{2I_{abs} \dot{x} [Cl_2]}{\phi} + \left\{ \frac{(1-\dot{x})^2 2 I_{abs}}{k_6 [Cl_2]} \right\}^{\frac{1}{2}} \right\}$$

$$= \frac{k_2 [A] k [Cl_2] (\dot{x} \tau_1 + (1-\dot{x}) \tau_2) 2I_{abs}}{k_\alpha + (k_\beta + k_\gamma) [Cl_2]}$$

where ϕ is the rate of diffusion of atoms to the wall, \dot{x} is the fraction of the chains terminated at the wall and τ_1 and τ_2 are the kinetic lifetimes of the linearly and mutually terminated chains respectively. \dot{x} was evaluated from the exponent of I_{abs} , τ_1 and τ_2 calculated from \dot{x} and τ and hence k_6 obtained from $k_6 [Cl_2] = (2I_{abs}(1-\dot{x}) \tau_2^2)^{-1}$.

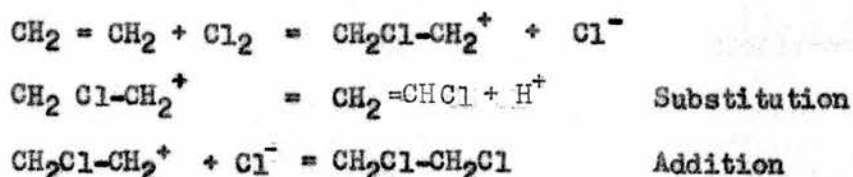
Chlorination of ethylene: The study of the chlorination of ethylene has been complicated by the occurrence of an appreciable dark reaction even at low temperatures and apparently due to some kind of surface process. In the

presence of excess oxygen Norrish and Jones⁶⁴ found that 200 mm. each of chlorine and ethylene reacted to completion in 30-40 mins. in the dark in clean glass vessels whereas in paraffin wax coated vessels less than 0.1% reaction occurred in 12 hours. Those authors also found that the reaction on clean glass was catalysed by water vapour but that water vapour had no effect on the reaction in the paraffin wax coated vessel. They believed that the rate was not affected by the condensation of dichloroethane in contrast with the observation of Stewart and Smith^{65,66} that the condensation of product enhanced the reaction rate and that the addition of dichloroethane or trichloroethane catalysed the reaction, particularly in the absence of oxygen. Stewart and Smith's experiments were carried out at 20°C with pure, dry reactants in an oxygen free system and they found an inhibition period followed by autocatalysis and that substitution as well as addition occurred. The substitution was inhibited by oxygen and believed to be "induced" by the addition reaction due to the formation of an unstable intermediate, $C_2H_4Cl_2^\ddagger$, which could react with chlorine or be deactivated by oxygen or the wall:



Brooks and Humphrey⁶⁷ found that the substitution did not occur if the reaction was kept cold and Rust and Vaughan⁶⁸, who reacted ethylene and chlorine in a flow system over a wide temperature range (200-480°C), found that substitution increased with increasing temperature. At low temperatures where there was little substitution the rate of reaction was approximately given by $R \propto [Cl_2] [C_2H_4]^{1/2}$ although increasing surface area increased the reaction rate "probably as a result of catalysed bimolecular association as

well as initiation of chains". Both addition and substitution were catalysed by tetraethyl lead and the catalysed reaction was suppressed by oxygen and therefore probably involved a free radical mechanism, but there was a residual addition reaction presumed due to molecular association at the surface. Below 150°C Groll et.al.⁶⁹ found that little reaction occurred in the liquid phase and Taft⁷⁰ suggested that the liquid phase reaction was ionic:



This idea was elaborated by Kuriacose and co-workers⁷¹ who investigated the chlorination in solution and explained their results by assuming that both substitution and addition occurred from the start of the reaction by an ionic mechanism. They also suggested that as a result of the exothermicity of the addition process chlorine atoms were produced which could initiate radical chain substitution in the olefine or solvent.

The most recent study of the thermal reaction is that of Chaikin⁷² who used differential calorimetry to determine the degree of heterogeneity of the reaction between 150 and 250°C. He found rate $\propto [\text{Cl}_2][\text{C}_2\text{H}_4]$ both in the presence and absence of oxygen and that the rate was insensitive to S/V ratio in the absence of oxygen but dependent on the ratio in the presence of oxygen. In agreement with this the temperature difference between the centre of the reaction vessel and its surface indicated that the reaction in the oxygen free system was entirely homogeneous and the results were explained in terms of chain centres being generated on the surface and destroyed in the interior of the reaction vessel, the low rate at high oxygen pressures being due to

rapid removal of the chain centres by oxygen before they can move far from the wall.

The gas phase photochemical reaction was studied at room temperature by Stewart and Weidenbaum⁷³ who assumed that long chains were involved since explosion could be induced by suitably adjusting the conditions. They found the rate law $-\frac{d[Cl_2]}{dt} = kI_{abs}[Cl_2]$ which suggests that termination is by linear removal of $C_2H_4Cl\cdot$ radicals. In competitive experiments with hydrogen the ratio of dichloroethane to hydrogen chloride formed was 80:1 from which it was concluded that the activation energy for the ethylene/chlorine reaction was $1.4 \text{ kcal.mole}^{-1}$ assuming that the difference in the two rates was entirely due to the activation energy difference.

In the temperature range 25-40°C and at pressures of 100-400 mm. Schmitz et al.⁷⁴ obtained a different rate expression:

$$R_{C_2H_4Cl_2} = k (I_{abs})^{\frac{1}{2}} [Cl_2] [C_2H_4]^{\frac{1}{2}}$$

and explained it in terms of a mechanism analogous to that for the formation of phosgene with a thermal equilibrium $C_2H_4Cl\cdot \xrightleftharpoons{4} C_2H_4 + Cl\cdot$ so that $k = k_3 / (k_7 K_{C_2H_4Cl\cdot})^{\frac{1}{2}}$. As already pointed out, this mechanism is impossible due to the high bond strength $D(C_2H_4 - Cl)$. They could not study the reaction at higher temperatures because of a rapid thermal reaction.

The photochlorination of ethylene was reinvestigated by Dainton, Lomax and Weston⁷⁵ at 25 and 35°C. The dark reaction was more important than with dichloroethylene and was about 2% of the photochemical rate at the lowest intensities and pressures used. Chromatographic and infra-red analyses showed that dichloroethane was the only product formed. The intensity exponent was found to be 0.65-0.75 depending on the diameter of the light beam, suggesting that loss of chain centres at the wall was occurring and, although below 70 mm.

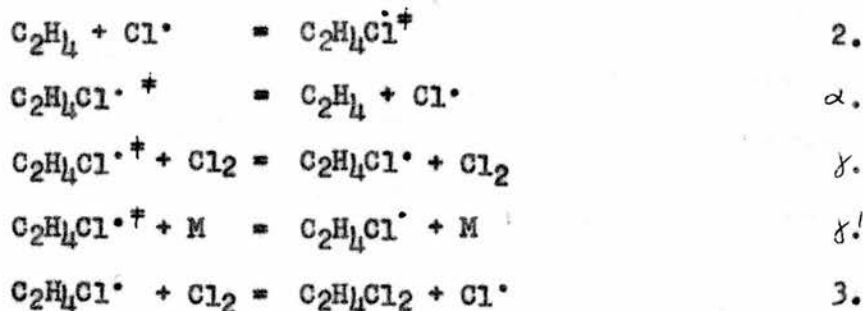
of ethylene the rate was proportional to the square root of the ethylene pressure, the chlorine pressure dependence was more complicated than the simple linear relationship suggested by Schmitz et al. The occurrence of some wall termination is not surprising in view of the high quantum yield of about 10^6 moles einstein⁻¹.

The authors suggest that for absorbed light intensities of about 4×10^{13} quanta l⁻¹.sec.⁻¹ and chlorine and ethylene pressures of about 50 mm. each, the rate law for the entirely homogeneous reaction would be

$$R_p = k_0 (I_{\text{abs}})^{\frac{1}{2}} [\text{C}_2\text{H}_4]^{\frac{1}{2}} [\text{Cl}_2] / (a + b [\text{Cl}_2])^{\frac{1}{2}} \quad \text{I.16}$$

Assuming the same mechanism postulated by Dainton et al. for the chlorination of dichloroethylene, $a/b = k_\alpha / (k_\beta + k_\gamma)$ and the experimental value of 2.9×10^{-3} is three times the corresponding ratio for the dichloroethylene system and suggests that k_α must be greater for ethylene since $(k_\beta + k_\gamma)$ would not be expected to vary very much.

Hagopian^{51,52} studied the competitive chlorination of ethylene and propane at 35°C. He found an appreciable dark reaction producing dichloroethane in a pyrex reaction vessel and that this dark reaction, presumed to be a bimolecular association on the surface, was inhibited by small pressures of chloro-derivatives but accelerated by larger pressures as suggested by earlier work^{65,66}. In urea-formaldehyde coated vessels the dark reaction was negligibly small and a study was made of the dependence of the ratio dichloroethane: propyl chlorides formed in the photochemical reaction. This ratio was found to increase with pressure of chlorine and of ethylene and was probably independent of propane pressure. A mechanism similar to that proposed by Dainton et al. for dichloroethylene was adopted:



This scheme contrasts with that of Dainton in allowing for collisional deactivation by species other than Cl_2 and by disregarding the atom exchange reactions β and δ . The pressure dependencies found suggest that $\text{C}_2\text{H}_4\text{Cl}^\cdot$ is collisionally deactivated by chlorine and ethylene but not by propane. Assuming the usual mechanism for the chlorination of propane, the following equation was used:

$$m \sum_{\text{T.P.R.}}^{\text{D.C.E.}} = \frac{k_2}{k_2^a} \left[\frac{k_\delta [\text{Cl}_2] + k_{\delta'} [\text{M}]}{k_\alpha + k_\delta [\text{Cl}_2] + k_{\delta'} [\text{M}]} \right]$$

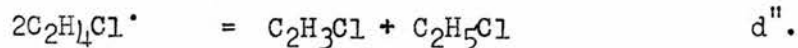
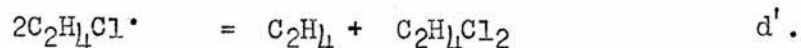
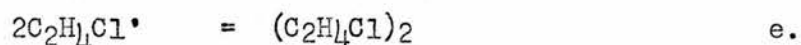
$$\text{where } m \sum_{\text{T.P.R.}}^{\text{D.C.E.}} = \frac{[1.2 \text{ Dichloroethane formed}] [\text{Propane}]_{\text{mean}}}{[\text{total propyl chlorides formed}] [\text{ethylene}]_{\text{mean}}}$$

and k_2^a is the sum of the rate constants for the formation of the n propyl and iso propyl radicals.

By working at high pressures where $(k_\delta [\text{Cl}_2] + k_{\delta'} [\text{C}_2\text{H}_4]) \gg k_\alpha$ the value of k_2/k_2^a was obtained at a series of temperatures in the range 294-457°K and k_2 calculated from the known value of k_2^a ³⁴. The Arrhenius plot obtained was curved and the interpretation somewhat uncertain but, by taking the asymptotic value of the slope at low temperatures a value of $\log k_2 = 10.6 \pm 0.3 - \frac{(584 \pm 540)}{2.303RT}$ derived. The resulting value of $\log k_2$ at 308°K ($\log k_2 = 10.16 \pm 0.1$) is in good agreement with the value obtained by Martens⁵² although Martens

found no evidence for wall effects or a hot radical mechanism in the competitive chlorination of ethylene with methylchloride or ethane.

In a recent study of the combination and disproportionation of chloroethyl and trichloromethyl radicals, produced by photolysing carbon tetrachloride in the presence of ethylene, Roquitte and Wijnen⁷⁶ found that the main products were 1,4 dichlorobutane, 1,3,3,3 tetrachloropropane and hexachloroethane which were presumably formed in radical combination reactions. Smaller amounts of chloroform, chloroethane and chloroethylene were detected and attributed mainly to disproportionation. For the chloroethyl radical the following mutual reactions occur:



and measurement showed that $k_e > 10k_d'$ or $10k_d''$. Hot radicals preferentially disproportionate⁷⁷ but no evidence was obtained to suggest that reactions involving excited chloroethyl radicals contributed to the product distribution. However, at the relatively high pressures used collisional deactivation of excited radicals will occur rapidly and such effects would not be observable within the limits of accuracy of the experiments.

Chlorination of vinyl chloride: In an early investigation of the photochemical formation of trichloroethane from vinyl chloride and chlorine, Schmitz and Schumacher⁷⁸ found that the rate was given by $R = k I_a^{\frac{1}{2}} [Cl_2]$. The reaction was shown to be a chain process with a quantum yield of about 10^5 moles einstein⁻¹ and was strongly inhibited by oxygen. There was no appreciable dark reaction.

The later results of Dainton, Lomax and Weston⁷⁵ were in good agreement and those workers also showed that at lower pressures the reaction rate was

dependent on olefine pressure and directly proportional to the square root of olefine pressure for pressures of less than 35 mm. This was explained in terms of the replacement of 8. by 7. as the main chain terminating stop. The mechanism proposed was identical to that adopted for the chlorination of dichloroethylene so that, when termination is entirely by 7.

$$R_p = (2I_a)^{\frac{1}{2}} k_3 [Cl_2] \left(\frac{k_2 [A] k_f}{k_7 k_3 (k_\alpha + \{k_\beta + k_f\} [Cl_2])} \right)^{\frac{1}{2}} \quad I.17$$

At high olefine pressures where termination is by 8.

$$R_p = \left(\frac{2I_a}{k_8} \right)^{\frac{1}{2}} k_3 [Cl_2] \quad I.18$$

and the use of the rotating sector technique allowed the evaluation of the Arrhenius parameters of 3. and 8.

Vinyl chloride was chlorinated in competition with cis-dichloroethylene⁷⁹ and the results interpreted as providing support for the excited radical mechanism on the basis of which it was shown that

$$R = \frac{d[A^a Cl_2]/dt [A^b]}{d[A^b Cl_2]/dt [A^a]} \left\{ 1 + \frac{k_\alpha^a + k_\beta^a [Cl_2]}{k_f^a [Cl_2]} \right\} = \frac{k_2^a}{k_2^b} \left\{ \frac{1 + k_\beta^b + \frac{k_\alpha^b}{k_f^b [Cl_2]}}{k_f^b [Cl_2]} \right\} \quad I.19$$

where the superscripts a and b refer to cis dichloroethylene and vinyl chloride respectively. The reactions were allowed to proceed to about 8% decomposition and the products analysed by gas chromatography after distilling off the excess chlorine and, by using the known values of k_α^a , k_β^a and k_f^a , the L.H.S. of equation I.19 was evaluated for a range of chlorine pressure and plotted against $[Cl_2]^{-1}$. As expected, the graphs were straight lines having small intercepts

at $[Cl_2]^{-1} = 0$ and from which $\frac{k_2^a}{k_2^b} \left\{ \frac{1 + k_\beta^b}{k_f^b} \right\}$ and $\frac{k_2^a}{k_2^b} \left\{ \frac{k_\alpha^b}{k_f^b} \right\}$

and hence $\frac{k_\alpha^b}{k_\beta^b + k_f^b}$ could be evaluated. R was found to be independent of

temperature within the range 30-65°C and E_2^b was taken as being equal to E_2^a by assuming that the terms within the brackets have the same temperature dependence. By further assuming that $k_\alpha : k_\beta : k_\gamma$ cannot be markedly structure dependent A_2^b was taken as being equal to A_2^a .

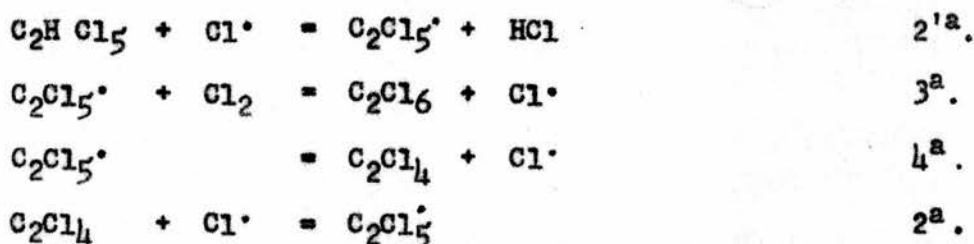
Chlorination of Trichloroethylene: Müller and Schumacher⁶² investigated this reaction in the temperature range 80-115°C and found it to be very similar to the chlorination of dichloroethylene and vinylchloride: the quantum yield was high (~ 700 moles einstein⁻¹), the reaction was inhibited by oxygen and above a limiting pressure of olefine (5 mm. in this case) the rate law was $R = k I_{abs}^{\frac{1}{2}} [O_2]$. From the temperature coefficient of the reaction E was (5.3 ± 0.3) kcal.mole⁻¹.

The same rate law was obtained by Dainton, Lomax and Weston⁸⁰ in the temperature range 22.5 - 112.5°C for pressures of trichloroethylene greater than 16 mm., although there was some indication that at low light intensities the exponent of I_{abs} was greater than 0.5, probably due to a small amount of linear termination. The dark reaction was shown to be negligible and the rotating sector technique used to determine the chain lifetime and hence evaluate k_8 and k_3 . The overall activation energy was estimated to be (4.9 ± 0.1) kcal.mole⁻¹, in good agreement with the value of Müller and Schumacher. At lower pressures of olefine the rate was dependent on the pressure, linearly so at less than 8 mm. and this was regarded as being due to the replacement of 8. by 7. and finally by 6. as the chain ending step.

Trichloroethylene was chlorinated competitively with cis-dichloroethylene⁷⁹ in experiments similar to those outlined above for vinyl chloride and with exactly analogous results. The activated radical scheme was again applied and the Arrhenius parameters for 2. shown to be the same for all three olefines

within the limits of error. In both sets of experiments the L.H.S. of the equation was independent of olefine pressure which again suggested that the radicals are not collisionally deactivated by the olefine.

Huybrechts et.al.⁴⁵ extended the temperature range to 500°K to check the conditions for the occurrence of the radical decomposition (4) and the radical-atom chain breaking step (7). At temperatures above 410°K, however, instead of a continuous decrease in pressure a pressure minimum was observed followed by a pressure maximum and a second pressure decrease and this was explained by including the following additional reactions :



The system was followed in detail by a combined manometric and mass spectrometric technique and the complex rate constant ratios $k_3/k_8^{\frac{1}{2}}$, $k_3\left\{\frac{k_2}{k_1k_7}\right\}^{\frac{1}{2}}$,

k_2^{a}/k_2 and $\frac{k_2^{\text{a}}k_4}{k_3k_2}$ were determined by using the appropriate steady state

equations. Using the known values of k_8 ⁷⁹ and k_2^{a} ⁵⁰ the equilibrium constant for the process $\text{C}_2\text{HCl}_4^\bullet \xrightleftharpoons[2]{4} \text{C}_2\text{HCl}_3 + \text{Cl}^\bullet$ was calculated: $\log k_4/k_2 = 3.97 - 20,400/4.57T$.

This gave $D(\text{C}_2\text{HCl}_3 - \text{Cl}) = 20.4 \text{ k.cal.mole}^{-1}$.

$\log k_2$ was calculated to be (9.75 ± 0.3) in reasonable agreement with Dainton's value⁸⁰ and the resulting value of A_4 was $5.0 \times 10^{13} \text{ sec}^{-1}$. The value of A_4 falls within the "normal" range for a unimolecular decomposition and the value of $E_4 = D(\text{C}_2\text{HCl}_3 - \text{Cl})$ is clearly that for the thermally equilibrated

radical and the authors concluded that there was no evidence for the hot radical mechanism postulated by Dainton.

Chlorination of Tetrachloroethylene: Dickinson and co-workers chlorinated tetrachloroethylene in solution⁸¹ and in the vapour phase⁸² and obtained the usual rate law : $-d[Cl_2]/dt = k I_{abs}^{\frac{1}{2}} [Cl_2]$ - and practically identical rate constants for the two systems. There was very little dark reaction, oxygen was a strong inhibitor and the quantum yield varied from 300 - 2,500 moles einstein⁻¹ depending on the conditions. In the vapour phase system hexachloroethane was deposited on the walls of the reaction vessel. The rate law was confirmed by Schott and Schumacher⁸³ and they determined an activation energy of 7.35 k.cal.mole⁻¹.

The photochlorination of tetrachloroethylene has been extensively studied by Goldfinger and co-workers^{47,50,84,85} who explain their results in terms of reactions 1-4, 7. and 8. of the general scheme. They claim that the atom-atom chain breaking step 6. does not occur and it follows that :

$$\frac{-d[Cl_2]}{dt} = (2I_{abs})^{\frac{1}{2}} k_3 [Cl_2] \left\{ k_8 + \frac{k_7 (k_4 + k_3 [Cl_2])}{k_2 [C_2Cl_4]} \right\}^{-\frac{1}{2}} \quad I.20$$

At low temperatures $k_8 \gg \frac{k_7 (k_4 + k_3 [Cl_2])}{k_2 [C_2Cl_4]}$

and at high temperatures $\frac{k_7 (k_4 + k_3 [Cl_2])}{k_2 [C_2Cl_4]} \gg k_8$ and $k_4 \gg k_3 [Cl_2]$

and the low and high temperature rate laws are respectively

$$\frac{-d[Cl_2]}{dt} = \left\{ \frac{2 I_{abs}}{k_8} \right\}^{\frac{1}{2}} k_3 [Cl_2] \quad I.21$$

and $\frac{-d[Cl_2]}{dt} = \left\{ \frac{2 I_{abs} k_2}{k_7 k_4} \right\}^{\frac{1}{2}} [Cl_2] [C_2Cl_4]^{\frac{1}{2}} \quad I.22$

The change in mechanism was actually observed experimentally in a static system in which the reaction was followed manometrically and, by direct photometric measurement of the chlorine concentration, $k_3/k_8^{1/2}$ and $k_3(k_2/k_7k_4)^{1/2}$ were evaluated in steady light and k_8 in intermittent light so that k_3 and k_7k_4/k_2 could also be calculated^{84,85}. From the temperature dependence of those constants and assuming $E_7 = 0$ and $D(C_2Cl_4 - Cl) = E_4$, $D(C_2Cl_4 - Cl)$ was estimated to be 16.8 k.cal.mole⁻¹ which again suggests that $C_2Cl_5^{\cdot}$ is not a vibrationally excited radical.

The competitive chlorination of methane and the chloromethanes against tetrachloroethylene was also investigated by Goldfinger's group in the temperature range 360 - 475°K. Where R_s and R_a are the rates of substitution and addition, respectively,

$$\frac{R_s}{R_a} = \frac{k_2' [RH]}{k_2 [C_2Cl_4]} \frac{1}{(1 + k_4/k_3 [Cl_2])} \quad I.23$$

and thus k_2'/k_2 and k_3k_2'/k_2k_4 and hence k_2 and k_3/k_4 were obtained (by using the values of k_2' given by Knox⁴⁸).

The pentachloroethyl radical may be formed either by abstraction of a hydrogen atom from pentachloroethane or by addition of a chlorine atom to tetrachloroethylene and a combination of the results from the chlorination of the two compounds separately with those from their competitive chlorination allowed a number of cross checks to be made on the rate constants of the elementary reactions involved⁵⁰.

The agreement was very satisfactory and indicated that the radicals formed from pentachloroethane and tetrachloroethylene are identical and, therefore, that a hot radical mechanism does not operate in the chlorination of tetrachloroethylene.

Chlorination of Fluoroethylenes: The photochlorinations of 1,1 difluoroethylene⁸⁶, chlorotrifluoroethylene^{87,88,89} and tetrafluoroethylene^{89,90} have been investigated and found to exhibit the high quantum yields, oxygen inhibition and low temperature coefficients characteristic of the photochlorination of the chloroethylenes. The rate laws, too, are similar: the rate is independent of olefine pressure, directly proportional to the chlorine pressure and, in the first two cases, to the square root of the absorbed light intensity. With tetrafluoroethylene the exponent of I_{abs} was found to be 0.67 and this was attributed to a certain amount of linear termination, an idea supported by the increased rate of reaction in the presence of 200 mm. CO_2 . Adopting the usual reaction mechanism and assuming the activation energy of the chain terminating steps to be zero, E_3 was found to be 1.9, 2.3 and 1 k.cal.mole⁻¹, respectively.

The rate of photochlorination of Bromotrifluoroethylene⁹¹ was satisfactorily described by $R = k I_{abs}^{\frac{1}{2}} [Cl_2]$ and was not measurably affected by the olefine pressure or by the presence of an added inert gas. The results were explained on the basis of the usual chain mechanism although some exchange must occur between chlorine and bromine atoms to form $CFCl = CF_2$ since the product distribution was found to be: $CF_2Cl \cdot CFClBr$ 60%, $CFCl_2 \cdot CF_2Cl$ 20% and $CF_2Br \cdot CFClBr$ 20%.

Chlorination of Higher Olefines^{68,69,92}: The study of those systems has been complicated by the occurrence of an extensive dark reaction particularly in the presence of a liquid phase. The reaction presumably takes place on the surface and its rate and the amount of substitution relative to addition increase whilst the temperature at which substitution becomes greater than addition decreases with the length and with branching of the hydrocarbon chain.

Although the reactions are inhibited by oxygen and occur in part via a free radical chain, the low temperature dark reaction almost certainly involves an ionic mechanism^{70,71}.

Information on the detailed mechanism and kinetics of those reactions is limited. Hagopian and Knox^{51,52} chlorinated propylene and isobutene in competition with propane and confirmed the presence of a strong heterogeneous component in the chlorination of olefines. The rate of dark formation of addition product was considerably lower in a urea-formaldehyde coated vessel and this made it possible to make a quantitative study of the photochemical reaction: the dark rate was found to increase with increase in the total hydrocarbon pressure and by extrapolating the ratio

$$\frac{[\text{addition product formed}] [\text{Propane}] \text{ mean}}{[\text{isopropyl chloride formed}] [\text{olefine}] \text{ mean}}$$

to zero dark time and zero hydrocarbon pressure the true ratios of k_2/k_2' were found and hence the values of k_2 were calculated from the known value of k_2' as $k_2(\text{Cl} + \text{C}_4\text{H}_8) = 10.62 \pm 0.2$ and $k_2(\text{Cl} + \text{C}_3\text{H}_6) = 10.20 \pm 0.1$ at 25°C.

Roselli and Schumacher⁹³ have recently investigated the gas phase photochlorination of 2-perfluorobutene and found that surface effects are not important. They showed that the reaction was inhibited by oxygen, had a quantum yield of 285 mole einstein⁻¹ and that the rate was given by $R = k I_{\text{abs}}^{\frac{1}{2}} [\text{Cl}_2]$. From the temperature coefficient of the overall rate, assuming the usual mechanism and taking $E_8 = 0$, E_3 was found to be (5.95 ± 0.45) k.cal.mole⁻¹.

5(d). General Features of Olefine Chlorination and Applicability of the Propane/Dichloroethylene system.

In the absence of surface effects many features of olefine chlorination

can be explained by the general reaction scheme already discussed and interpreted in terms of equations of the form of I.12. The Arrhenius parameters for the elementary reactions involved are not markedly structure sensitive except in the case of reaction 3. for which the activation energy increases regularly with n in the series $C_2Cl_n H_{4-n}$, n = 0-4. The predominating termination step is determined by the ratio $[Cl^\bullet] / [ACl^\bullet] = (k_3[Cl_2] + k_4) / k_2[A]$ and $E_2 < E_3 \ll E_4$ so that at high olefine pressures when this ratio is ^{low} high termination is entirely by 8., the rate law becomes

$$- \frac{d [Cl_2]}{dt} = k (2I_{abs})^{\frac{1}{2}} [Cl_2] \quad \text{where } k = k_3 / k_8^{\frac{1}{2}}$$

and rate laws of this form have been obtained for all the substituted olefines discussed above. At lower olefine pressures the other terms in the denominator of I.12 become important and the rate shows a dependence on olefine pressure below a limiting pressure. In the chloroethylene series the limiting pressure decreases with increasing chlorine content as a result of the increase in E_3 . This increase in E_3 is also responsible for the corresponding decrease in quantum yield and chain length.

At higher temperatures 4. competes increasingly with 3., the ratio $[Cl^\bullet] / [ACl^\bullet] = (k_4 + k_3 [Cl_2]) / k_2 [A]$ increases with temperature as a result of which 7. replaces 8. as the chain terminating reaction and the rate law is given by equation I.22. This behaviour has been observed for trichloroethylene and tetrachloroethylene and the value of D (A - Cl) calculated from k_4 found to be in satisfactory agreement with those obtained from pyrolysis studies. A rate law of the form I.22 is obtained at much lower temperature for the photosynthesis of phosgene as a result of the low value of D (CO - Cl).

The experiments of Dainton et al. on dichloroethylene, however, have

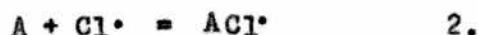
shown convincingly that this simple mechanism is inadequate, and the suggestion by Dainton that the radical ACl^{\bullet} is formed in a vibrationally excited state and can undergo a characteristic series of reactions (α, β, γ) has been used to explain his results on the chlorination of dichloroethylene, vinyl chloride, trichloroethylene and ethylene and a similar scheme was applied by Hagopian and Knox to results on the chlorination of ethylene.

Incorporating the excited radical reactions in the mechanism $[Cl^{\bullet}] / [ACl^{\bullet}]$ becomes $\left\{ \frac{k_2 [A] k_{\alpha}}{k_3 [Cl_2] (k_{\alpha} + (k_{\beta} + k_{\gamma}) [Cl_2])} \right\}^{-1}$ instead of $\left\{ k_2 [A] / k_3 [Cl_2] \right\}^{-1}$ and

the general form of I.12 remains the same and reduces to equivalent equations under specified conditions for both schemes - compare equations I.13 - I.18 with I.20 - I.22. It is not surprising, therefore, that early investigations carried out by following pressure changes did not reveal the inadequacies of the general scheme.

The overall position remains unsatisfactory: Dainton et.al. have observed hot radical effects for all the chloroethylenes apart from tetrachloroethylene whereas Goldfinger's group obtained values of E_h for tetrachloroethylene and trichloroethylene which suggest that the radical is thermally equilibrated. There is also doubt about the exact properties of the excited radical: Dainton et.al. found that it was collisionally deactivated by chlorine but not by the olefine and that atom transfer reactions occur whereas Hagopian and Knox found collisional deactivation by both reactants but did not make allowance for atom transfer reactions.

In order that the Arrhenius parameters of the reaction



in the series $A = C_2Cl_nH_{4-n}$ for $n = 0 - 4$ may be used as a test of transition

state theory it is essential that the rate constants be known with certainty and this is impossible as long as there is doubt about the reaction mechanism.

If the simple mechanism operates the competitive chlorination of an olefine and a saturated hydrocarbon will obey the equation

$$\frac{-d[A]}{dt} / \frac{-d[RH]}{dt} = \frac{k_2 [A]}{k_2' [RH]} \quad \text{I.24}$$

$$\therefore \frac{d[A]}{k_2 [A]} = \frac{d[RH]}{k_2' [RH]} \quad \text{I.25}$$

and by integration

$$\frac{k_2}{k_2'} = \frac{\ln([A]_i/[A]_f)}{\ln([RH]_i/[RH]_f)} \quad \text{I.26}$$

where *i* and *f* refer to the initial and final pressures respectively.

For small amounts of reaction the approximation may be made that

$$\ln [A]_i / \ln [A]_f = \frac{\Delta[A]}{[A]_i} \quad \text{and} \quad \ln [RH]_i / \ln [RH]_f = \frac{\Delta[RH]}{[RH]_i}$$

$$\therefore \frac{k_2}{k_2'} = \frac{\Delta[A] \cdot [RH]_i}{\Delta[RH] \cdot [A]_i} = R_s^a$$

and, provided the chains are long

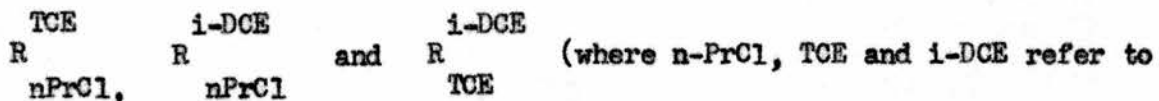
$$R_s^a = \frac{[ACl_2] [RH]_i}{[RCl] [A]_i} \quad \text{I.27}$$

where $[ACl_2]$ and $[RCl]$ are the concentrations of chlorinated products.

The independence on reactant pressures of this ratio at a given temperature

should be a delicate test of the reaction mechanism. The propane/dichloro-

ethylene system was chosen since the radical decomposition can be directly observed by following the isomerisation reaction and the presence of which at low temperatures would, in itself, indicate that the general scheme was invalid. If this were true a study of the change in the product functions



n-propyl chloride, tetrachloroethane and either cis or trans dichloroethylene respectively) with reactant pressures should elucidate the reaction mechanism and make it possible to devise a kinetic expression from which values of k_2/k_2' could be obtained. By carrying out such investigations over a temperature range it would then be possible to obtain the Arrhenius parameters of reaction 2. for cis and for trans dichloroethylene by utilising the known values of A and E for the attack of a chlorine atom at the primary hydrogens in propane.

CHAPTER II.

EXPERIMENTAL

1. Materials

Chlorine was obtained from an I.C.I. cylinder. The middle fraction was collected and freed from water by several distillations from a trap at -80°C to the trap of a 2 litre storage bulb at $-19\frac{1}{2}^{\circ}\text{C}$ and was then exhaustively degassed.

Propane was obtained from an I.C.I. cylinder and was purified as above.

It was found to contain:

C_2	0.2%
C_3H_6	0.3%
C_3H_8	97.9%
iso C_4H_{10}	1.6%

Cis and Trans 1,2 Dichloroethylene were prepared from B.D.H. Technical Grade 1,2 dichloroethylene. The crude material was distilled and the fractions boiling in the ranges 47.2°C to 47.8°C and 59.9°C to 60.3°C collected and redistilled on a 1 metre column packed with glass helices. The trans dichloroethylene fraction boiling in the range 46.5°C to 47.0°C was taken and the only impurity detectable by gas chromatography was cis dichloroethylene, present in less than 0.001%. Cis dichloroethylene was collected in the boiling range 60.05°C to 60.15°C and was found by gas chromatographic analysis to contain 0.01% trans dichloroethylene together with a small amount ($<0.01\%$) of a second, unidentified impurity which was eluted between the two isomers.

The purified compounds were stored in dark bottles in the presence of a small amount of hydroquinone which was shown to prevent isomerisation on standing. Samples for current use were exhaustively degassed and kept in traps on the apparatus at -194°C .

Cis and Trans 1,2 Dibromoethylene were prepared from B.D.H. Lab. Reagent Grade 1,2 dibromoethylene by preparative scale gas chromatography on a 3ft. x 1 in. column of 25% Tween 60 on 40-60 mesh celite at 57°C . Each was identified by its refractive index and stored in a trap on the apparatus.

The refractive indices and purities of the samples were:

	$n_D^{17.5}$	Lit. value ⁹⁴	Impurity
cis dibromoethylene	1.5430	1.54312	2% trans.
trans dibromoethylene	1.5506	1.55054	2% cis.

Oxygen was taken from a B.O.C. cylinder.

Nitrosyl Chloride⁹⁵: 100 ml. 50% hydrochloric acid was dropped onto a stirred solution of 14g. sodium nitrite and 33g. potassium iodide in a 3-necked 1 litre flask. The NO_2 formed by mixing the NO evolved from the reaction with a stream of air was condensed out at -194°C and was then converted to NOCl by being passed up a tower of moist potassium chloride. The NOCl was fractionally distilled in the vacuum system to remove HCl , degassed in the usual manner and stored in a 2 litre bulb.

Carbon Dioxide: Commercial "Drikold" was used. It was freed from condensable impurities, degassed and stored in the same way as chlorine.

n Propyl Chloride: B.D.H. Reagent Grade material was purified by preparative

scale gas chromatography on a 3ft. x 1 in. column (25% dinonyl phthalate on firebrick). The product was analysed by gas chromatography and no detectable impurity was found.

iso Propyl Chloride: as for n propyl chloride.

1,1,2,2 Tetrachloroethane: 500 ml. B.D.H. Technical Grade material was fractionally distilled on a 1 metre column, the middle 100 ml. being collected. It was analysed by gas chromatography and found to contain less than 1% impurities.

1,2 Dichloro 1,2 Dibromo Ethane: Departmental Ampoule.

t Butyl Chloride: B.D.H. Lab. Reagent.

iso Butyl Chloride: B.D.H. Lab. Reagent.

1,2 Dichloropropane: B.D.H. Lab. Reagent.

Hydrogen was taken from a B.O.C. cylinder and was purified by passing over activated molecular sieve (type 5A).

Celite: 80-100 mesh G-Cel Plain supplied by Gas Chromatography Limited.

Tween 60: supplied by L. Light & Company Limited.

Silicone Oil: M & B. Embaphase Grade.

2. Apparatus

The experimental work was carried out in a conventional high vacuum apparatus and the reaction products were analysed by temperature programmed gas chromatography. It is convenient to describe the apparatus under the headings: a) kinetic system b) analysis system.

a) Kinetic System (see fig.II.1). The apparatus was constructed from pyrex glass and was evacuated by means of two separate vacuum lines. The mercury diffusion pumps on the two lines were both backed by the same "Speedivac" rotary oil pump and a vacuum of about 10^{-6} mm Hg was obtained as measured on a simple mercury vacuostat. Greased high vacuum taps were used on the vacuum lines but were replaced by metal valves with teflon seats and glands (manufactured by F.J. Hone Limited, 19 Eldon Park, London, S.E.25) in the rest of the apparatus. Those valves had the advantage of a small dead volume and they also avoided problems arising from the solubility of highly chlorinated reaction products in tap grease. The glass/metal seals were made by tightening a coupling nut on a polythene sleeve (see Fig.II.2).

Storage of Materials. The reactants and oxygen were introduced into the system via removable trap 1 and stored in the bulbs and traps on manifold 1. The storage bulbs were equipped with attached pump-down traps and the reactants were exhaustively degassed each morning. Nitrosyl chloride was introduced via removable trap 3 and was stored in the 2 litre bulb on manifold 3. Care was taken to exclude the NOCl from the reactant and reaction part of the system (manifolds 1 and 2) and manifold 3 was evacuated by a separate vacuum line.

Pressure Measurement. The pressure of the reactant gases was measured with a pyrex spiral gauge (fig. II.3). The gauge was stabilised to vibration by

being immersed in liquid paraffin and by the use of a fine glass torque suspension. It had a mirror attached to it which reflected light from a projector lamp back to a centimetre scale and was calibrated against a mercury manometer, a good straight line relationship being obtained (fig.II.4):

$$2.34 \text{ scale cm} \approx 1 \text{ cm Hg.}$$

A second gauge, used for measuring pressures of NOCl , was found to have a calibration factor of 2 scale cm/cm Hg.

Mixing Vessel. The darkened mixing vessel had a volume of 300 ml. and was equipped with a side arm which could be used for condensing gases or, alternatively, heated to promote thermal mixing.

Reaction Vessel. The pyrex reaction vessel had a volume of 85 ml. and was entirely immersed in a thermostating vapour bath apart from a short capillary lead of negligibly small volume ($<.02$ ml) attaching it to the apparatus. The vapour bath was provided by the following boiling liquids, the temperatures being read on thermometers placed in a thermometer well which protruded into the vapour:

diethyl ether	$35 \pm 0.5^\circ\text{C.}$
benzene	$79.5 \pm 1.0^\circ\text{C.}$
chlorobenzene	$132.5 \pm 0.5^\circ\text{C.}$

The thermometers used to read the two lower temperatures were checked against National Physical Laboratory calibrated thermometers and that used to read the upper temperature was calibrated by means of a standard thermocouple. The reaction vessel was kept in a light-proof box and the thermometer well and vapour bath condenser were blackened to prevent stray light entering the system. Illumination of the reaction vessel was achieved via a removable

window in the box.

Illumination. The photochemical reaction was initiated by means of a 250 W. Mazda projector lamp. The light was passed through a 10% solution of copper sulphate in a 600 ml. beaker, which acted as a heat filter, and the intensity of the radiation incident on the reaction vessel could be adjusted by interspersing layers of wire gauze.

b) Analysis System (see fig.II.5). The reaction products (see next section) had boiling points ranging from 34.8°C to 146.2°C and in order to achieve a good separation in a reasonable time and to obtain chromatographic peaks suitable for accurate measurement it was necessary to use temperature programmed gas chromatography and, in this section, attention will be drawn to the modifications that this entailed in the otherwise conventional system.

Carrier Gas. Hydrogen was used as the carrier gas and it was found necessary to purify it by passing over activated molecular sieve (type 5A) otherwise extraneous broad peaks were obtained as the column temperature was raised. In order to maintain a constant flow rate as the temperature and hence the carrier gas viscosity and column back pressure increased a constant - differential type flow controller (model 63 BU-L manufactured by Moore Products Company, H. and Lycoming Sts., Philadelphia) was used in conjunction with a needle valve (Edwards High Vacuum). This arrangement maintained the flow rate constant to within $\pm 2\%$ over the temperature range 20°C - 160°C. The flow rate through the analytical column was measured continuously with a capillary flow meter which had a response of 1 cm. for a flow rate of 20.2 ml. H₂/min.

Columns. The carrier gas was split between the dummy and analytical columns

and then passed through the two sides of the detector. The columns were made of glass of 4 mm. internal diameter and in order to obtain a good base line with changing temperature they had to be evenly matched: details of the column packings used will be given in section II.3. The columns were housed in an oven, the temperature of which could either be maintained constant or increased at a predetermined rate as required (details of the oven and the ancillary thermostating and programming equipment are given in an appendix).

Detector. A Gow-Mac Model 9285 katharometer was used and the circuit diagram is given in fig.II.6. Four two-volt accumulators in conjunction with a variable resistance were employed to provide the Wheatstone bridge circuit with a constant 6V, corresponding to a bridge current of ~ 200 ma and the out-of-balance signal was fed to a Honeywell Brown 1mV recorder via an attenuator which had the following ranges available: 1, 2.01, 5.03, 9.99, 24.33, 49.7 and 100.0 mV. The katharometer was kept in an oven, thermostatted at $59 \pm 0.5^\circ\text{C}$ by means of a simple mercury - cut-off thermometer and valve relay (Electro Methods Limited, Stevenage. - Type No.213B). It was found that the vibration caused by the column oven fan motor upset the base line and this problem was overcome by mounting the katharometer oven on rubber pads. Before entering the katharometer the column gas streams were thermally equilibrated by passing through heat exchanges (3 ft. capillary copper tubing) maintained at the same temperature as the katharometer.

Injection. The reaction products were condensed into the liquid nitrogen cooled injection U-tube, the analytical column carrier gas stream diverted through the U-tube and the sample injected onto the column by rapidly replacing the liquid nitrogen flask with one of boiling water. Sharp injections were facilitated by heating the Hone valves of the injection system and the pre-column leads to a temperature of about 60°C .

3. Identification and Quantitative Analysis of Products

Identification of reaction products was accomplished by matching their retention times with those of authentic samples. In this way it was demonstrated that the only products from the chlorination of cis and of trans dichloroethylene were the isomeric olefine and 1,1,2,2 tetrachloroethane (up to 30% conversion) and, for small conversions (<10%) the only products from the chlorination of propane were isopropyl chloride, n propyl chloride and 1,2 dichloropropane. The latter was apparently produced by the addition of chlorine to the small amount of propylene present as impurity since the other dichloropropanes were not obtained. For higher percentage reaction five other products were formed in small amounts: two of them were identified from their retention times as t butyl chloride and iso butyl chloride (from the 1.6% iso butane impurity) and the other three were assumed to be 1,1 dichloropropane, 1,3 dichloropropane and 2,2 dichloropropane since, although pure samples were not available to check their retention times, the retention times did not match those of the products of the chlorination of iso propyl chloride and n propyl chloride.

For the quantitative study of the competitive chlorination of cis or trans dichloroethylene with propane the reactions were stopped before a maximum of 10% of any of the reactants had been consumed and under those conditions the only products obtained were isopropyl chloride, n propyl chloride, the isomeric olefine and 1,1,2,2 tetrachloroethane together with 1,2 dichloropropane from the propylene impurity. Gas chromatographic analysis of the reaction products was carried out on a column of 4 ft. 25% W/W Silicone oil on celite + 2 ft. 15% W/W Tween 60 on Celite. A carrier gas flow rate of 35 ml. H₂/min was used and the columns were maintained at 25°C for 15 mins. after the injection and then temperature programmed at 60°/min. to a maximum temperature of 160°C. Under

those conditions the retention times of the products (including minor and secondary products) were as follows:

<u>Compound</u>	<u>Retention Time (mins., secs.)</u>		<u>Boiling Point (°C)</u>
iso propyl chloride	6	30	30.8
t butyl chloride	8	10	50.7
n propyl chloride	9		47.2
trans dichloroethylene	13	30	47.7
iso butyl chloride	17		68.8
2,2 dichloropropane	17	40	70.5
cis dichloroethylene	20		60.25
1,1 dichloropropane	22		88.3
1,2 dichloropropane	23	20	95.6
1,3 dichloropropane	27	50	120.5
1,1,2,2 tetrachloroethane	33	30	146.2

The relative sensitivity of the detector to the various products was determined by analysing standard mixtures of two or three of them and comparing the peak areas. The peak areas were measured with a planimeter and were converted to areas measured on the 1 mV range and at a flow rate of 35 ml. H₂/min. by the following relationship:

$$\text{area (1 mV, 35 ml/min)} = (\text{measured area}) \times (\text{attenuation factor}) \times (\text{measured flow rate}/35)$$

The relative sensitivities were found to be:

iso propyl chloride	1.01
n propyl chloride	1
trans dichloroethylene	0.98
cis dichloroethylene	0.98
tetrachloroethane	1.07

It was unnecessary to know the absolute sensitivities to calculate the results of the competitive experiments but desirable in order that the total amount of reaction could be estimated. By using samples of known volume and pressure the absolute sensitivity for n propyl chloride was found to be:

33,900 planimeter units = 1 cm in reaction vessel at 20°C.

or 730 planimeter units = 1 μ mole.

4. Experimental Procedure

Preparation of Dichloroethylene/Propane Mixtures. The propane was degassed and manifold 1, manifold 2 and the mixing vessel evacuated. A pressure of propane was then measured into the mixing vessel, the excess frozen back into the storage bulb and the manifolds re-evacuated. The propane was condensed from the mixing vessel into one of the traps on manifold 1 and a similar procedure used to measure a pressure of dichloroethylene after which the propane was condensed back into the mixing vessel with the dichloroethylene and the vapours allowed to mix, thermal mixing being promoted by heating the side arm. Enough mixture was usually prepared for at least 10 runs. For convenience the hydrocarbon + olefine mixture will be referred to as the "Mix".

Preparation of Chlorine/Carbon Dioxide Mixtures. In a number of experiments carbon dioxide was added to the reaction mixture as an inert diluent and in those cases carbon dioxide/chlorine mixtures of the required composition were first prepared by a procedure similar to that above apart from the fact that in this case a 1 litre storage bulb was used as a mixing vessel.

Procedure for a Run. The kinetic apparatus was thoroughly evacuated and a pressure of Mix measured into the reaction vessel. The excess was frozen into the removable trap 1 and manifolds 1 and 2 re-evacuated before being filled with a pressure of chlorine of a magnitude calculated to give the desired pressure in the reaction vessel (in the experiments in which carbon dioxide was used the chlorine was replaced by the appropriate carbon dioxide/chlorine mixture). The valve to the reaction vessel was then opened, the pressure allowed to equilibrate, the valve reclosed and the excess chlorine condensed into removable trap 1. After allowing to mix for two minutes the

reaction mixture was illuminated for a time and with an intensity of light sufficient to give the desired amount of reaction (< 10% of any component used up). The required conditions were obtained by trial and error and were so adjusted that the illumination time was between 1 min. and 4 mins.

1 mm oxygen was measured into manifold 2 and 1 mm nitrosyl chloride into manifold 3. When sufficient reaction had occurred illumination was discontinued and the reaction inhibited by opening the taps to manifolds 2 and 3 in rapid succession. After 30 secs. the reaction products were condensed into the pump-down trap on manifold 3 at -194°C . Complete transference of the products was ensured by pumping through for 5 mins. and the excess chlorine, propane and carbon dioxide then distilled off at -120°C (melting alcohol). The exact procedure adopted, and particularly the times involved, depended to some extent on the composition of the reaction mixture but the general method was as follows: the pump-down trap was heated up to -120°C by immersing in melting alcohol after the valve to manifold 2 had been closed, the valve to vacuum was then opened and pumping continued for 20 mins. At the end of this time the vacuum valve was closed and the condensate evaporated to release occluded chlorine and then recondensed at -120°C before distilling to vacuum for a further 10 mins. to remove the remainder of the chlorine and the chlorine-free reaction products then transferred to the injection U-tube in preparation for analysis.

Inhibition Procedure and Removal of Chlorine. The chlorination of the dichloroethylene/propane mixture had an appreciable rate in room light and it was, therefore, necessary to inhibit the process to ensure that further reaction did not occur during the transference of the reaction products and the removal of excess chlorine by distillation. Oxygen and nitrosyl chloride are both

well established inhibitors of chlorination reactions⁹⁶ and nitrosyl chloride had already been used for a purpose identical to that in this work by Ayscough, Cocker and Dainton⁴⁶. In our work oxygen was used as inhibitor in manifold 2 to avoid getting NOCl into the kinetic part of the system and NOCl was used in manifold 3 and during the distillation because of the low solubility of oxygen at -120°C .

In order to check that reaction products were not lost during the removal of the excess chlorine, propane and carbon dioxide, a mixture was prepared in which the components were present in approximately the proportions expected from a reaction but with no chlorine present and submitted to the usual distillation procedure, the distillate being condensed out at -194°C and analysed. Apart from propane only traces of iso propyl chloride were obtained together with a small amount of the excess olefine. The excess olefine from the reaction did not enter into the calculations and chlorine atom attack at the primary position in propane was used as the competitive standard so that it was unnecessary to know the amounts of iso propyl chloride produced and the procedure was regarded as satisfactory. The reproducibility of the kinetic results using the procedures outlined above was of the order of $\pm 5\%$.

5. Calculation of Results. The product peak areas on the chromatographs were measured and converted to areas at the standard 1 mV and 35 ml.H₂/min. as indicated in section II.3. For the cis dichloroethylene/propane system it was necessary to correct the trans dichloroethylene area for the small amount of trans dichloroethylene present as impurity in the cis but the amount of cis present in the trans starting material was so small that corrections to the cis peak were unnecessary in studying the chlorination of trans dichloroethylene/propane mixtures.

The following functions were then calculated:

a) Cis Dichloroethylene/Propane System

$$\frac{R_{TCE}}{n \text{ PrCl}} = \frac{[TCE]_{\text{formed}} [PrH]_{\text{initial}}}{[n \text{ PrCl}]_{\text{formed}} [cDCE]_{\text{initial}}} \quad \text{II.1}$$

$$\frac{R_{tDCE}}{n \text{ PrCl}} = \frac{[tDCE]_{\text{formed}} [PrH]_{\text{initial}}}{[n \text{ PrCl}]_{\text{formed}} [cDCE]_{\text{initial}}} \quad \text{II.2}$$

$$\frac{R_{tDCE}}{R_{TCE}} = \frac{[tDCE]_{\text{formed}}}{[TCE]_{\text{formed}}} \quad \text{II.3}$$

Taking account of the calibration factors given in section II.3 and making allowance for the fact that the propane was 97.9% pure we have:

$$\frac{R_{TCE}}{n \text{ Pr Cl}} = \frac{\text{Area TCE}}{\text{Area n PrCl}} \times \frac{P_{PrH}}{P_{cDCE}} \times \frac{0.979}{1.07} \quad \text{II.4}$$

$$\frac{R_{tDCE}}{n \text{ PrCl}} = \frac{\text{Area tDCE}}{\text{Area n PrCl}} \times \frac{P_{PrH}}{P_{cDCE}} \times \frac{0.979}{0.98} \quad \text{II.5}$$

$$\frac{R_{tDCE}}{R_{TCE}} = \frac{\text{Area tDCE}}{\text{Area TCE}} \times \frac{1.07}{0.98} \quad \text{II.6}$$

where P_{PrH} and P_{cDCE} are the initial pressures of propane and cis dichloroethylene.

The functions $R_{t\text{DCE}}^{n\text{PrCl}}$ and $R_{e\text{DCE}}^{\text{TCE}}$ which were also investigated are simply the reciprocals of expressions II.5 and II.6.

b) Trans Dichloroethylene/Propane System

By analogy with a) we have

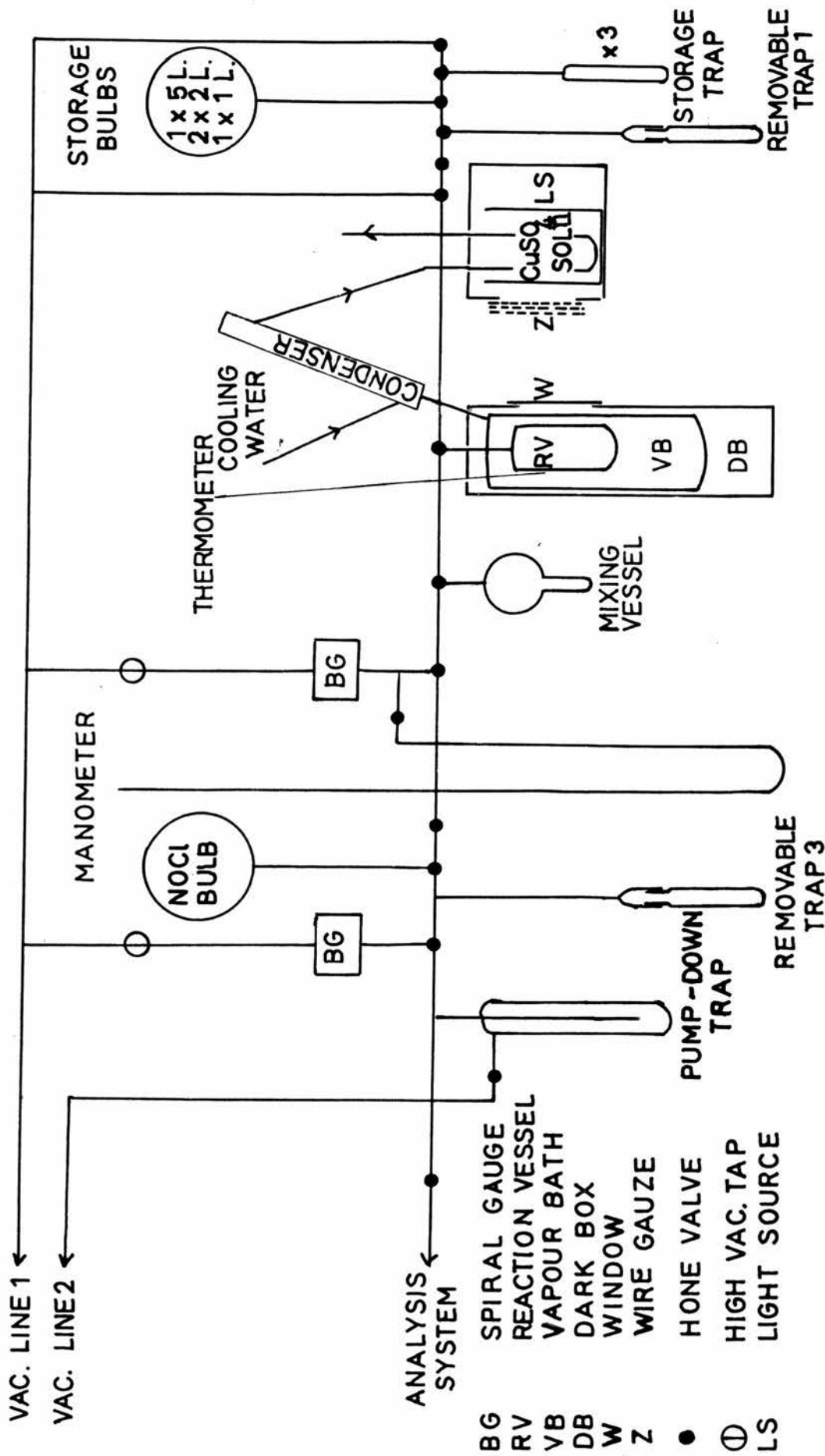
$$R_{n\text{PrCl}}^{\text{TCE}} = \frac{\text{Area TCE}}{\text{Area n PrCl}} \times \frac{P_{\text{PrH}}}{P_{t\text{DCE}}} \times \frac{0.979}{1.07} \quad \text{II.7}$$

$$R_{n\text{PrCl}}^{e\text{DCE}} = \frac{\text{Area eDCE}}{\text{Area n PrCl}} \times \frac{P_{\text{PrH}}}{P_{t\text{DCE}}} \times \frac{0.979}{0.98} \quad \text{II.8}$$

$$R_{\text{TCE}}^{e\text{DCE}} = \frac{\text{Area eDCE}}{\text{Area TCE}} \times \frac{1.07}{0.98} \quad \text{II.9}$$

where P_{PrH} and $P_{t\text{DCE}}$ are the initial pressures of propane and trans dichloroethylene.

The functions $R_{e\text{DCE}}^{n\text{PrCl}}$ and $R_{e\text{DCE}}^{\text{TCE}}$ are the reciprocals of II.8 and II.9.



MANIFOLD 1
MANIFOLD 2
MANIFOLD 3
KINETIC SYSTEM
FIG. 1

FIG. II.2

HONE VALVE

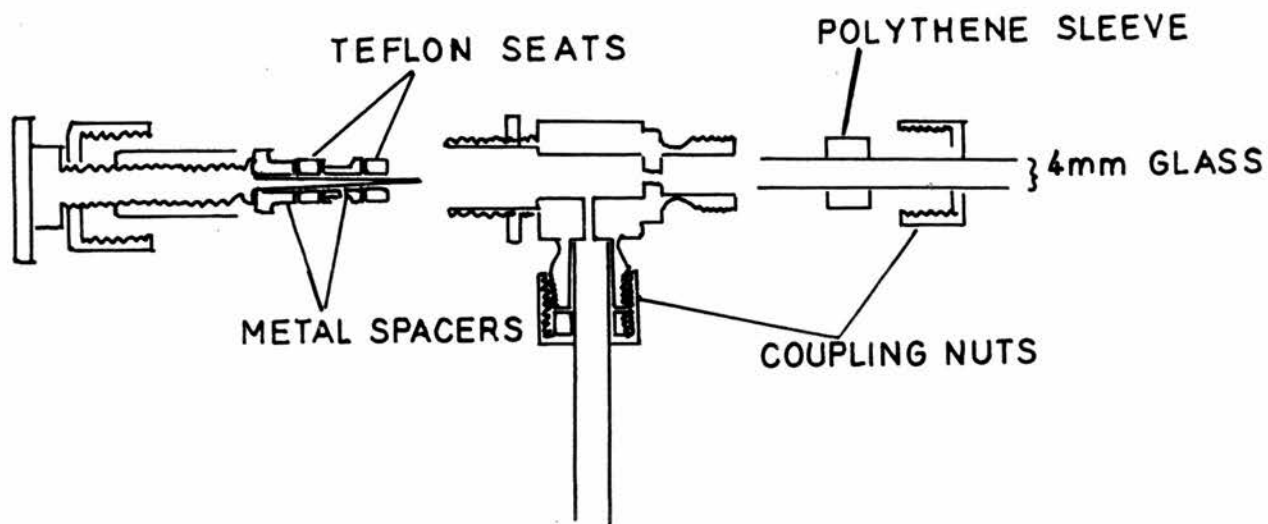
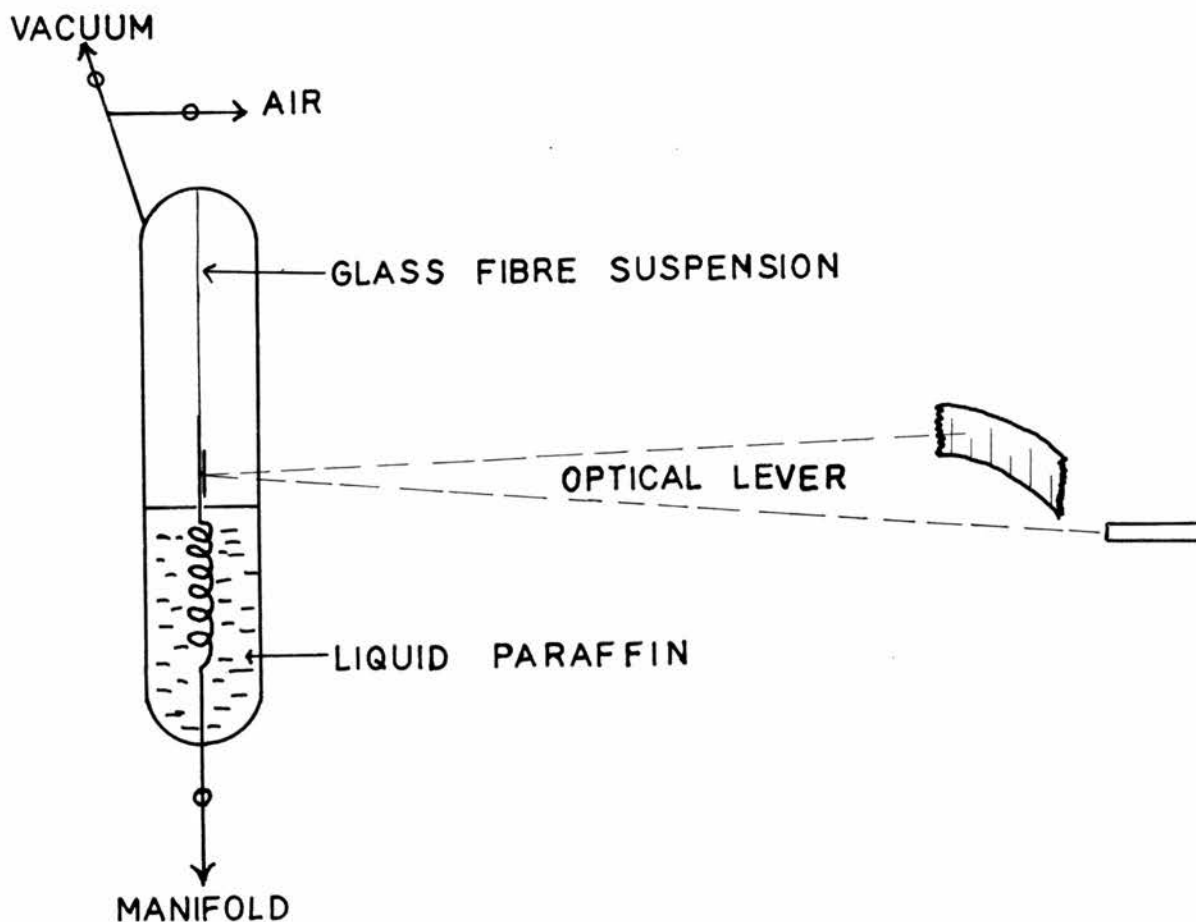
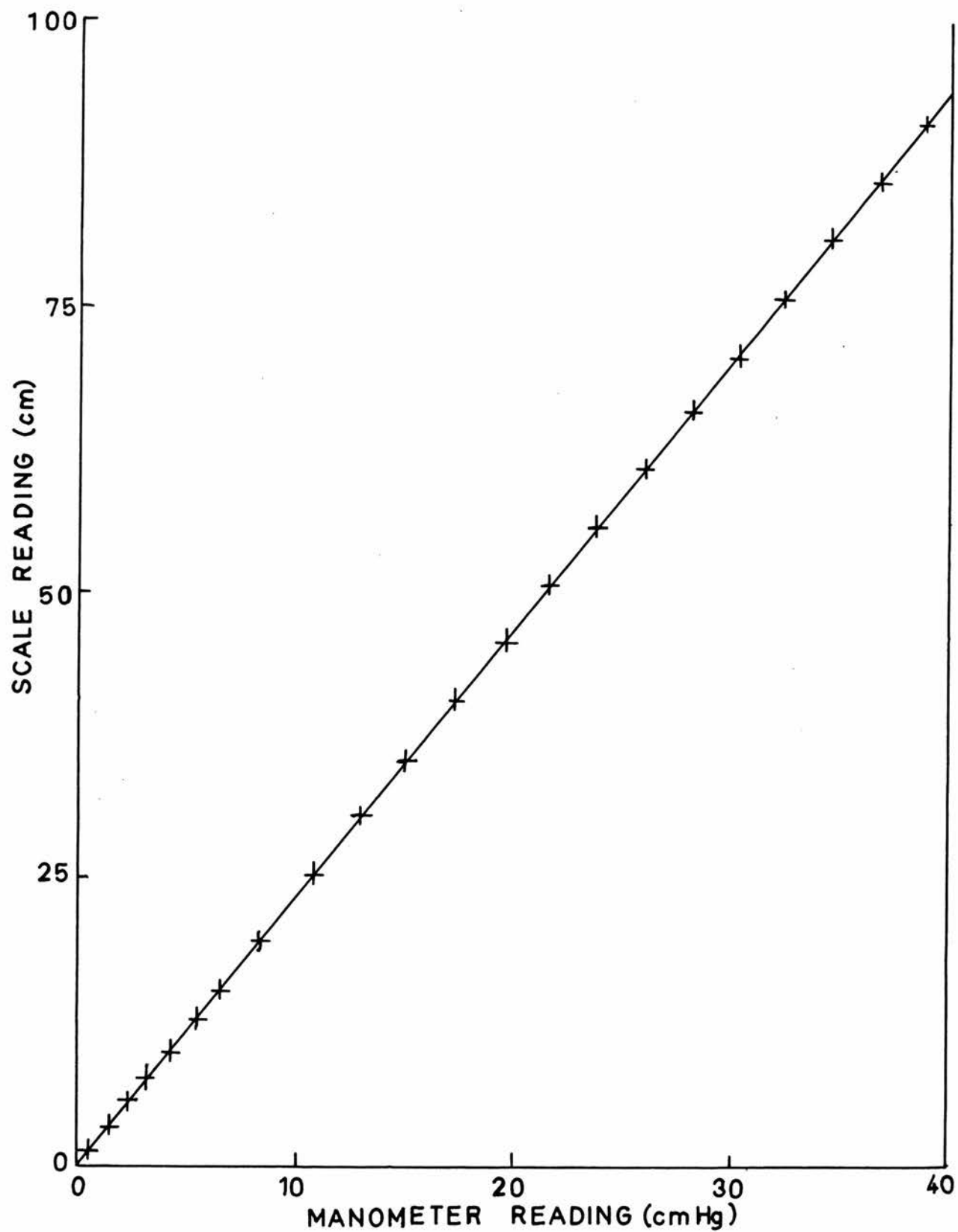


FIG. II.3

SPIRAL GAUGE

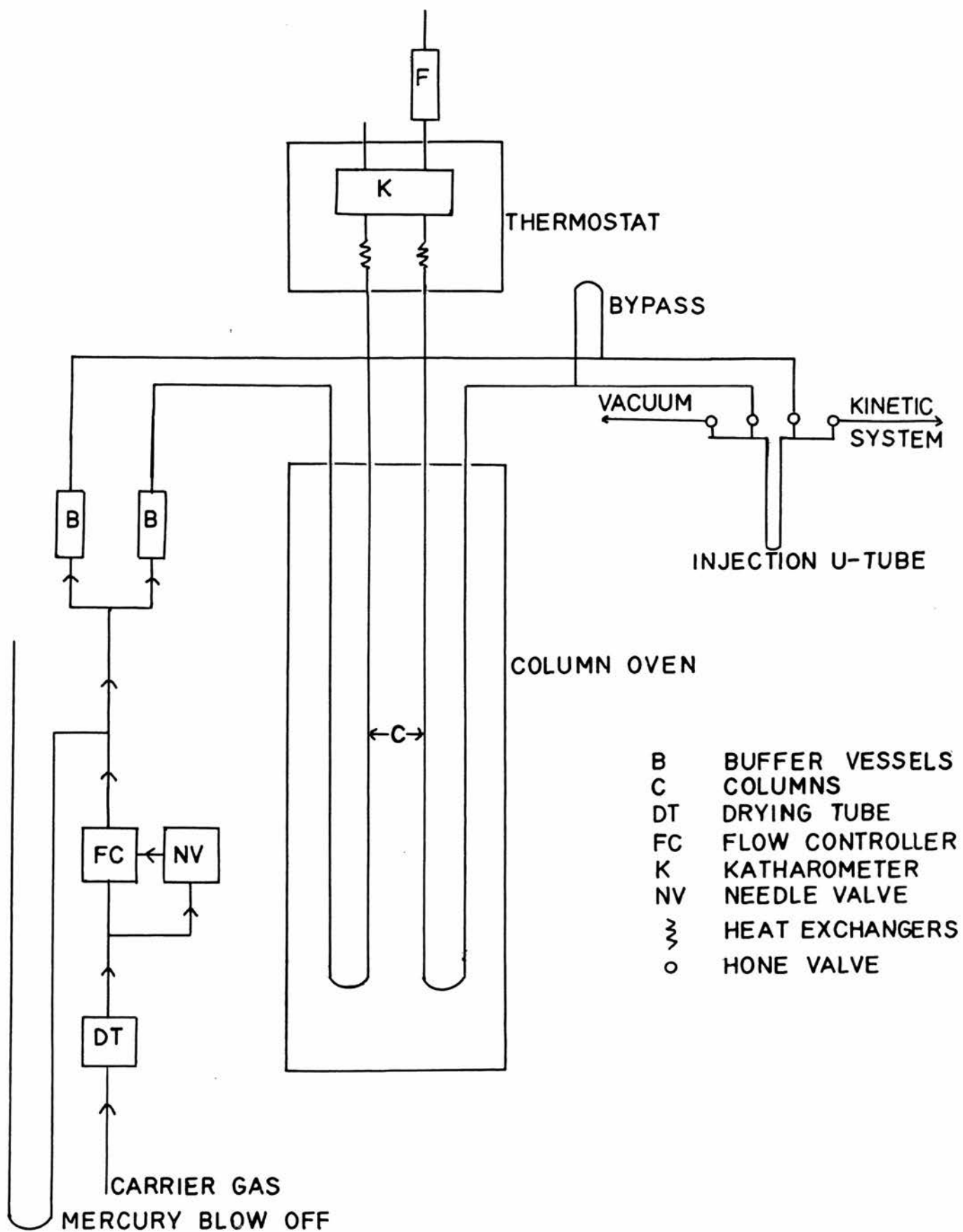


CALIBRATION OF SPIRAL GAUGE

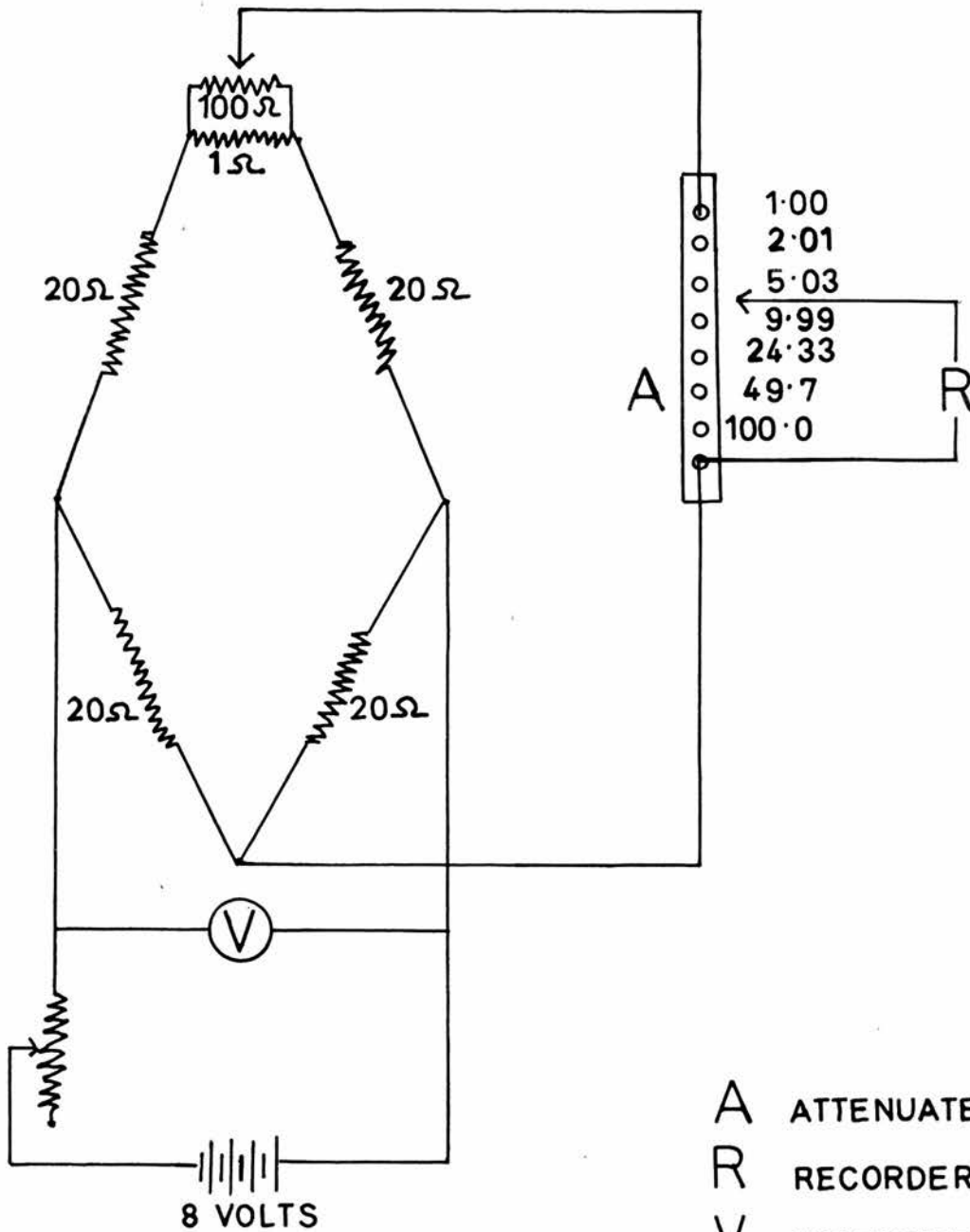


ANALYSIS SYSTEM

FIG. II.5



KATHAROMETER CIRCUIT

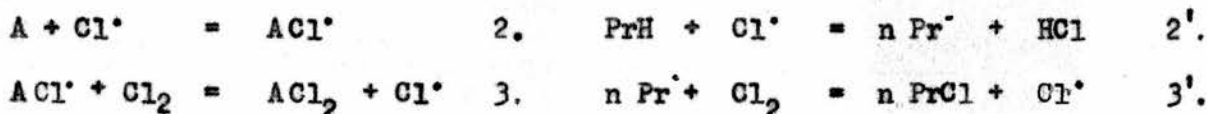


A ATTENUATER
R RECORDER
V VOLTMETER

CHAPTER III.

R E S U L T S

It was shown in the Introduction that if the propagating steps in the competitive chlorination of propane and dichloroethylene are:



and provided that the chains are long then $R_{n PrCl}^{TCE}$ should be independent of the pressure of the reactants. Furthermore, since the dissociation energy of the C — Cl bond in dichloroethylene is about 20 k.cal.mole⁻¹ ²⁸ reaction 4.



would not be expected to occur below ~ 160°C and isomerisation of dichloroethylene should not be observed at lower temperatures. As indicated in Chapter II, however, a considerable amount of isomer was detected in the reaction products, indicating the inadequacy of the above scheme. In an attempt to elucidate the reaction mechanism the variation of $R_{n PrCl}^{TCE}$, $R_{n PrCl}^{IDCE}$ and R_{TCE}^{IDCE} with reactant pressure was investigated: the range of conditions studied and an index of the corresponding tables and figures are given on page 62.

Notes: (1) Corresponding tables and figures are given the same number.

Where more than one figure refers to a particular table the additional figures are also given a coding letter and, for convenient reference, figures of a given type are coded in the same way and are presented in a group.

(2) Figures III.8a and III.8c and III.16a and III.16c. refer to all

the results for the *cis* dichloroethylene/propane and the *trans* dichloroethylene/propane systems respectively.

(3) Indistinguishable points on the figures are represented by concentric circles.

Competitive Chlorination of Cis Dichloroethylene and Propane at 79.5°C.

Reactant Pressure mm Hg		PrH	Cl ₂	CO ₂	PrH		Table Number	Figure Numbers
cDCE	cDCE				t	cDCE		
32.1	32.1	42.7	42.7	nil	1	III.1	—	
sum=64.1		42.7	42.7	nil	4.0 -0.25	III.2	III.2	
5.3-85.5	21.4	42.7	42.7	nil	1	III.3	III.3b, III.3e	
21.4	5.3-85.5	42.7	42.7	nil	4.0 -0.25	III.4	III.4b, III.4c	
5.3-85.5	21.4	42.7	42.7	nil	0.25-4.0	III.5	III.5b, III.5e	
21.4	21.4	21.4-342	42.7	nil	1	III.6	III.6a, III.6b, III.6e	
21.4	21.4	42.7	42.7	0-299	1	III.7	III.7b, III.7e	

+ Pre-illumination dark time varied from 2-30 mins.

Competitive Chlorination of Trans Dichloroethylene and Propane at 79.5°C.

Reactant Pressure mm Hg		PrH	Cl ₂	CO ₂	PrH		Table Number	Figure Numbers
tDCE	tDCE				t	cDCE		
32.1	32.1	42.7	42.7	nil	1	III.9	—	
sum=64.1		42.7	42.7	nil	4.0 -0.25	III.10	III.10	
5.3-85.5	21.4	42.7	42.7	nil	1	III.11	III.11b, III.11c	
21.4	5.3-85.5	42.7	42.7	nil	4.0 -0.25	III.12	III.12b, III.12e	
5.3-85.5	21.4	42.7	42.7	nil	0.25-4.0	III.13	III.13b, III.13c	
21.4	21.4	21.3-343	42.7	nil	1	III.14	III.14a, III.14b, III.14c	
21.4	21.4	42.7	42.7	0-299	1	III.15	III.15b, III.15c	

+ Pre-illumination dark time varied from 2-30 mins.

Table III. 1. Dependence of R on Dark Time

Propane Pressure = 32.1 mm Hg
 Cis - Dichloroethylene Pressure = 32.1 mm Hg Temp. = 79.5°C.
 Chlorine Pressure = 42.7 mm Hg
 Dark time = variable; illuminated for 4 mins.

Run No.	Dark time mins.	Area n-PrCl	Area t-DCE	Area TCE	t-DCE R n-PrCl	TCE R n-PrCl	t-DCE R TCE	TCE R t-DCE
13c	2	2077	650	1743	0.313	0.77	0.406	2.44
14c	"	2561	765	2042	0.299	0.73	0.408	2.43
15c	"	2233	655	1777	0.293	0.73	0.402	2.47
16c	"	2752	795	2204	0.289	0.74	0.394	2.52
105c	30	2454	736	2011	0.300	0.75	0.399	2.49
106c	"	2381	705	1901	0.296	0.73	0.404	2.45
107c	"	2202	663	1872	0.301	0.78	0.386	2.57
108c	"	2088	642	1708	0.307	0.75	0.409	2.42

Table III. 2. Dependence of R on Propane : Cis Dichloroethylene Ratio

Pressure of (Propane + Cis-Dichloroethylene) = 64.1 mm Hg

Pressure of Chlorine = 42.7 mm Hg Temp. = 79.5°C.

Propane : Cis-Dichloroethylene = variable

Run No.	PrH: c-DCE	Area n-PrCl	Area t-DCE	Area TCE	t-DCE R n-PrCl	TCE R n-PrCl	t-DCE R TCE	TCE R t-DCE
55e	4:1	3003	222	612	0.296	0.75	0.395	2.51
56e	"	3627	282	694	0.311	0.70	0.443	2.24
57e	"	2693	204	532	0.303	0.72	0.418	2.37
49e	2:1	4284	617	1730	0.288	0.74	0.389	2.55
50e	"	3528	522	1437	0.296	0.75	0.396	2.51
51e	"	3359	505	1319	0.301	0.72	0.418	2.38
13e	1:1	2077	650	1743	0.313	0.77	0.406	2.44
14e	"	2561	765	2042	0.299	0.73	0.408	2.43
15e	"	2233	655	1777	0.293	0.73	0.402	2.47
16e	"	2752	795	2204	0.289	0.74	0.394	2.52
36e	1:2	1766	1075	2710	0.304	0.70	0.432	2.29
37e	"	1482	863	2390	0.291	0.74	0.394	2.52
38e	"	1399	832	2242	0.298	0.73	0.404	2.45
58e	1:4	457	584	1481	0.319	0.74	0.430	2.31
59e	"	451	575	1549	0.319	0.79	0.405	2.45
60e	"	349	435	1145	0.311	0.75	0.415	2.40

Table III. 3. Dependence of R on
(Propane + Cis-Dichloroethylene) Pressure

Propane : Cis-Dichloroethylene = 1:1

Pressure of (Propane + Cis-Dichloroethylene) = variable. Temp. = 79.5°C.

Pressure of Chlorine = 42.7 mm Hg

Run No.	P _{Mix} mm Hg	1/P _{Mix} mm Hg ⁻¹ x10 ²	Area n-PrCl	Area t-DCE	Area TCE	t-DCE R n-PrCl	TCE R n-PrCl	t-DCE R TCE	TCE R t-DCE	n PrCl R t-DCE
1c	8.5	11.7	562	196	364	0.349	0.60	0.587	1.69	2.87
2c	"	"	216	755	146	0.349	0.62	0.563	1.76	2.86
3c	"	"	689	235	433	0.342	0.57	0.593	1.67	2.93
4c	"	"	663	233	452	0.357	0.62	0.562	1.76	2.85
5c	25.6	3.91	2241	726	1710	0.324	0.70	0.463	2.15	3.09
6c	"	"	1517	485	1088	0.320	0.66	0.486	2.04	3.13
7c	"	"	975	315	750	0.323	0.70	0.457	2.17	3.10
8c	"	"	1261	418	927	0.331	0.67	0.492	2.02	3.02
9c	42.7	2.34	2149	669	1669	0.311	0.71	0.437	2.27	3.21
10c	"	"	1971	640	1527	0.324	0.71	0.456	2.17	3.08
11c	"	"	2028	638	1565	0.315	0.71	0.444	2.23	3.18
12c	"	"	1955	603	1423	0.308	0.67	0.461	2.15	3.24
13c	64.1	1.56	2077	650	1743	0.313	0.77	0.406	2.44	3.20
14c	"	"	2561	765	2042	0.299	0.73	0.408	2.43	3.35
15c	"	"	2233	655	1777	0.293	0.73	0.402	2.47	3.41
16c	"	"	2752	795	2204	0.289	0.74	0.394	2.52	3.46
17c	85.5	1.17	2454	702	2136	0.286	0.80	0.358	2.77	3.50
18c	"	"	3271	901	2752	0.276	0.77	0.357	2.78	3.63
19c	"	"	2682	728	2467	0.272	0.84	0.316	3.08	3.68
20c	"	"	2680	763	2281	0.284	0.78	0.364	2.72	3.51
21c	128.2	0.780	3163	814	3010	0.257	0.87	0.295	3.36	3.89
22c	"	"	3045	815	2949	0.268	0.89	0.301	3.62	3.74
23c	"	"	2893	751	2793	0.260	0.88	0.293	3.38	3.85
24c	"	"	2511	662	2521	0.264	0.89	0.286	3.47	3.79
25c	170.9	0.585	3138	769	3460	0.243	1.01	0.242	4.09	4.08
26c	"	"	1628	403	1884	0.248	1.06	0.233	4.25	4.04
27c	"	"	2204	516	2497	0.234	1.04	0.226	4.40	4.27
28c	"	"	2354	532	2474	0.227	0.97	0.234	4.23	4.42

Table III. 4. Dependence of R on Cis-Dichloroethylene Pressure

Pressure of Propane = 21.4 mm Hg
 Pressure of Cis-Dichloroethylene = variable Temp. = 79.5°C.
 Pressure of Chlorine = 42.7 mm Hg

Run No.	P _{c-DCE} mm Hg	1/P _{c-DCE}	Area n-PrCl	Area t-DCE	Area TCE	t-DCE		TCE		n PrCl	
		mm Hg ⁻¹ x10 ²				R n-PrCl	R n-PrCl	R TCE	R t-DCE	R t-DCE	
29c	5.3	18.7	2852	233	460	0.327	0.59	0.552	1.80	3.06	
30c	"	"	2478	198	421	0.319	0.62	0.513	1.93	3.13	
31c	"	"	2319	188	391	0.324	0.62	0.524	1.89	3.08	
32c	10.7	9.36	2555	415	925	0.325	0.66	0.490	2.03	3.08	
33c	"	"	2390	392	815	0.328	0.63	0.524	1.89	3.05	
34c	"	"	2981	502	1039	0.336	0.64	0.527	1.88	2.97	
35c	"	"	2552	404	912	0.317	0.65	0.483	2.05	3.16	
9c	21.4	4.67	2149	669	1669	0.311	0.71	0.437	2.27	3.21	
10c	"	"	1971	640	1527	0.324	0.71	0.456	2.17	3.08	
11c	"	"	2028	638	1565	0.315	0.71	0.444	2.23	3.18	
12c	"	"	1955	603	1423	0.308	0.67	0.461	2.15	3.24	
36c	42.7	2.34	1766	1075	2710	0.304	0.70	0.432	2.29	3.28	
37c	"	"	1482	863	2390	0.291	0.74	0.394	2.52	3.43	
38c	"	"	1399	832	2242	0.298	0.73	0.404	2.45	3.36	
+ 39c	85.5	1.17	153	175	535	0.286	0.80	0.356	2.78	3.50	
+ 40c	"	"	146	175	533	0.300	0.83	0.358	2.77	3.34	
+ 41c	"	"	257	304	958	0.296	0.85	0.346	2.87	3.38	
+ 42c	"	"	195	230	713	0.295	0.84	0.352	2.82	3.39	

+ Part of reaction mixture analysed.

Table III. 5. Dependence of R on Propane Pressure

Pressure of Propane = variable
 Pressure of Cis-Dichloroethylene = 21.4 mm Hg Temp. = 79.5°C
 Pressure of Chlorine = 42.7 mm Hg

Run No.	P _{PrH} mm Hg	1/P _{PrH} mm Hg ⁻¹ x10 ²	Area n-PrCl	Area t-DCE	Area TCE	t-DCE	TCE	t-DCE	TCE	n-PrCl
						R n-PrCl	R n-PrCl	R TCE	R t-DCE	R t-DCE
43e	5.3	18.7	354	470	995	0.332	0.64	0.515	1.93	3.01
44e	"	"	359	458	987	0.319	0.63	0.518	1.96	3.14
45e	"	"	339	444	907	0.327	0.61	0.534	1.86	3.05
46e	10.7	9.36	1526	983	2217	0.322	0.66	0.484	2.05	3.10
47e	"	"	1880	1191	2688	0.317	0.65	0.483	2.05	3.16
48e	"	"	1879	1174	2576	0.312	0.63	0.493	2.00	3.20
9e	21.4	4.67	2149	669	1669	0.311	0.71	0.437	2.27	3.21
10e	"	"	1971	640	1527	0.324	0.71	0.456	2.17	3.08
11e	"	"	2028	638	1565	0.315	0.71	0.444	2.23	3.18
12e	"	"	1955	603	1423	0.308	0.67	0.461	2.15	3.24
49e	42.7	2.34	4284	617	1730	0.288	0.74	0.389	2.55	3.47
50e	"	"	3528	522	1437	0.296	0.75	0.396	2.51	3.38
51e	"	"	3359	505	1319	0.301	0.72	0.418	2.38	3.33
52e	85.5	1.17	2792	206	615	0.295	0.81	0.365	2.72	3.39
53e	"	"	3246	235	712	0.290	0.80	0.360	2.76	3.45
54e	"	"	2934	209	624	0.285	0.78	0.365	2.72	3.51

Table III. 6. Dependence of R on Chlorine Pressure

Propane Pressure = 21.4 mm Hg
 Cis Dichloroethylene Pressure = 21.4 mm Hg Temp. = 79.5°C.
 Chlorine Pressure = variable

Run No.	P _{Cl₂} mm Hg	1/P _{Cl₂} mm Hg ⁻¹ x10 ²	Area n-PrCl	Area t-DCE	Area TCE	t-DCE	TCE	t-DCE	TCE	n-PrCl
						R n-PrCl	R n-PrCl	R TCE	R t-DCE	R t-DCE
61e	21.4	4.67	603	188	426	0.312	0.65	0.481	2.06	3.21
62e	"	"	540	189	365	0.350	0.62	0.564	1.76	2.86
63e	"	"	701	236	475	0.337	0.62	0.542	1.83	2.97
9e	42.7	2.34	2149	669	1669	0.311	0.71	0.437	2.27	3.21
10e	"	"	1971	640	1527	0.324	0.71	0.456	2.17	3.08
11e	"	"	2028	638	1565	0.315	0.71	0.444	2.23	3.18
12e	"	"	1955	603	1423	0.308	0.67	0.461	2.15	3.24
64e	87.2	1.15	2230	645	2025	0.289	0.83	0.348	2.86	3.46
65e	"	"	1335	398	1257	0.298	0.86	0.347	2.87	3.35
66e	"	"	1766	528	1662	0.298	0.86	0.347	2.86	3.34
67e	128	0.78	1054	286	1058	0.272	0.92	0.295	3.37	3.69
68e	"	"	695	186	731	0.268	0.96	0.278	3.58	3.74
69e	"	"	1460	389	1538	0.267	0.96	0.276	3.60	3.75
70e	"	"	1892	544	2103	0.286	1.02	0.282	3.52	3.48
71e	164	0.61	2329	631	2517	0.271	0.99	0.274	3.65	3.69
72e	"	"	2400	665	2695	0.277	1.03	0.269	3.69	3.61
73e	"	"	2218	583	2507	0.261	1.03	0.254	3.91	3.80
74e	214	0.466	1793	454	2111	0.252	1.08	0.235	4.23	3.95
75e	"	"	1648	374	2017	0.227	1.12	0.203	4.91	4.41
76e	"	"	1232	309	1430	0.251	1.06	0.236	4.32	3.99
77e	278	0.360	9658	2202	12640	0.227	1.19	0.190	5.22	4.39
78e	"	"	2152	514	2812	0.239	1.20	0.199	4.98	4.19
79e	"	"	2313	537	2786	0.233	1.12	0.210	4.72	4.31
80e	342	0.292	3460	690	5122	0.199	1.35	0.147	6.75	5.01
81e	"	"	1859	375	2908	0.202	1.43	0.141	7.05	4.96
82e	"	"	2353	429	3579	0.194	1.39	0.131	7.59	5.48

Table III. 7. Dependence of R on Carbon Dioxide Pressure

Pressure of Propane = 21.4 mm Hg
 Pressure of Cis Dichloroethylene = 21.4 mm Hg
 Pressure of Chlorine = 42.7 mm Hg
 Pressure of Carbon Dioxide = variable
 Temp. = 79.5°C.

Run No.	P _{CO2} mm Hg	1/P _{CO2} mm Hg ⁻¹ x10 ²	Area n-PrCl	Area t-DCE	Area TCE	t-DCE		TCE		n-PrCl	
						R	R	R	R	R	R
9e	0	-	2149	669	1669	0.311	0.71	0.437	2.27	3.21	
10e	0	-	1971	640	1527	0.324	0.71	0.456	2.17	3.08	
11e	0	-	2028	638	1565	0.315	0.71	0.444	2.23	3.18	
12e	0	-	1955	603	1423	0.308	0.67	0.461	2.15	3.24	
83e	42.7	2.34	530	159	432	0.300	0.73	0.410	2.47	3.33	
84e	"	"	1863	545	1502	0.292	0.74	0.395	2.51	3.42	
85e	"	"	2172	659	1663	0.304	0.70	0.432	2.30	3.30	
86e	85.5	1.17	3048	885	2666	0.290	0.80	0.362	2.74	3.44	
87e	"	"	3007	894	2673	0.296	0.81	0.365	2.72	3.36	
88e	"	"	2810	801	2463	0.286	0.80	0.354	2.79	3.51	
89e	128	0.78	1005	303	922	0.301	0.84	0.358	2.77	3.17	
90e	"	"	1300	376	1191	0.289	0.84	0.344	2.88	3.46	
91e	"	"	1361	373	1229	0.274	0.83	0.331	3.00	3.65	
92e	"	"	1755	507	1554	0.289	0.81	0.335	2.79	3.46	
93e	171	0.585	2756	740	2698	0.269	0.89	0.299	3.32	3.72	
94e	"	"	3118	817	3153	0.262	0.93	0.282	3.51	3.82	
95e	"	"	2479	669	2357	0.270	0.87	0.309	3.21	3.71	
96e	235	0.426	2846	737	3052	0.259	0.98	0.263	3.77	3.86	
97e	"	"	1883	484	2129	0.257	1.03	0.248	3.96	3.89	
98e	"	"	2802	717	2972	0.256	0.97	0.263	3.77	3.91	
99e	"	"	2811	765	3025	0.272	0.98	0.276	3.60	3.67	
100e	299	0.334	1490	312	1809	0.209	1.11	0.188	5.28	4.78	
101e	"	"	1521	348	1595	0.229	0.96	0.238	4.17	4.37	
102e	"	"	4892	1069	6165	0.219	1.15	0.189	5.25	4.58	
103e	"	"	2254	511	2418	0.227	0.98	0.230	4.31	4.41	
104e	"	"	3183	817	3983	0.257	1.14	0.224	4.44	3.89	

Table III. 9. Dependence of R on Dark Time

Pressure of Propane = 32.1 mm Hg
 Pressure of Trans-Dichloroethylene = 32.1 mm Hg Temp. = 79.5°C.
 Pressure of Chlorine = 42.7 mm Hg
 Dark time = variable; illuminated for 4 mins.

Run No.	Dark Time mins.	Area n-PrCl	Area c-DCE	Area TCE	c-DCE	TCE	c-DCE	TCE
					R n-PrCl	R n-PrCl	R TCE	R c-DCE
10t	2	3382	2798	1745	0.83	0.47	1.75	0.57
11t	"	2502	1920	1251	0.77	0.46	1.67	0.59
12t	"	1089	871	567	0.80	0.48	1.68	0.59
13t	"	3536	2873	1704	0.81	0.44	1.84	0.54
14t	"	3688	2858	1928	0.78	0.48	1.62	0.61
97t	30	3820	3140	1946	0.82	0.47	1.74	0.56
98t	"	3288	2596	1507	0.79	0.42	1.88	0.53
99t	"	3437	2812	1651	0.82	0.44	1.85	0.54
100t	"	3689	2849	1862	0.77	0.46	1.67	0.59

Table III. 10. Dependence of R on
Propane : Trans-Dichloroethylene Ratio

Propane : Trans-Dichloroethylene = 1:1
 Pressure of (Propane + Trans-Dichloroethylene) = 64.1 mm Hg Temp. = 79.5°C.
 Pressure of Chlorine = 42.7 mm Hg

Run No.	PrH: t-DCE	Area n-PrCl	Area c-DCE	Area TCE	c-DCE	TCE	c-DCE	TCE
					R n-PrCl	R n-PrCl	R TCE	R c-DCE
50t	4:1	4297	850	591	0.79	0.50	1.57	0.63
51t	"	6168	1238	755	0.80	0.45	1.79	0.55
52t	"	6172	1283	822	0.83	0.49	1.70	0.58
44t	2:1	4280	1690	1055	0.80	0.48	1.65	0.57
45t	"	4330	1680	962	0.78	0.43	1.80	0.55
46t	"	4196	1661	1064	0.79	0.47	1.70	0.58
10t	1:1	3382	2798	1745	0.83	0.47	1.75	0.57
11t	"	2502	1920	1251	0.77	0.46	1.67	0.59
12t	"	1089	871	567	0.80	0.48	1.68	0.59
13t	"	3536	2873	1704	0.81	0.44	1.84	0.54
14t	"	3688	2858	1928	0.78	0.48	1.62	0.61
32t	1:2	1966	3138	1928	0.80	0.45	1.77	0.56
33t	"	1240	1931	1223	0.78	0.45	1.72	0.58
34t	"	1073	1779	1167	0.83	0.50	1.66	0.60
53t	1:4	919	2854	2017	0.78	0.50	1.54	0.64
54t	"	552	1674	1145	0.76	0.47	1.59	0.62
55t	"	867	2759	1932	0.79	0.51	1.56	0.63

Table III. 11. Dependence of R on
(Propane + Trans-Dichloroethylene) Pressure

Propane: Trans-Dichloroethylene = 1:1
 Pressure of (Propane + Trans-Dichloroethylene) = variable. Temp. = 79.5°C
 Pressure of Chlorine = 42.7 mm Hg

Run No.	R _{Mix} mm Hg	1/P _{Mix} mm Hg ⁻¹ x10 ²	Area n-PrCl	Area c-DCE	Area TCE	c-DCE R n-PrCl	TCE R n-PrCl	c-DCE R TCE	TCE R c-DCE	n-PrCl R c-DCE
1t	8.5	11.7	879	866	308	0.98	0.32	3.07	0.324	1.02
2t	"	"	1104	1045	388	0.95	0.32	2.94	0.338	1.06
3t	"	"	825	743	270	0.90	0.30	3.00	0.331	1.11
4t	25.6	3.91	2098	1941	913	0.92	0.40	2.31	0.428	1.08
5t	"	"	1871	1618	803	0.86	0.39	2.20	0.452	1.16
6t	"	"	2065	1843	916	0.89	0.40	2.19	0.452	1.12
7t	42.7	2.34	2412	2117	1181	0.88	0.45	1.96	0.51	1.14
8t	"	"	3130	2542	1428	0.81	0.42	1.94	0.51	1.23
9t	"	"	2898	2453	1332	0.85	0.42	2.06	0.49	1.18
10t	64.1	1.56	3382	2798	1745	0.83	0.47	1.75	0.57	1.21
11t	"	"	2502	1920	1251	0.77	0.46	1.67	0.59	1.30
12t	"	"	1089	871	567	0.80	0.48	1.68	0.59	1.25
13t	"	"	3536	2873	1704	0.81	0.44	1.84	0.54	1.23
14t	"	"	3688	2858	1928	0.78	0.48	1.62	0.61	1.29
15t	85.5	1.17	2013	1476	1123	0.73	0.51	1.43	0.69	1.36
16t	"	"	1895	1432	1018	0.76	0.49	1.54	0.65	1.32
17t	"	"	1544	1173	837	0.76	0.50	1.53	0.65	1.32
18t	"	"	1564	1218	830	0.78	0.49	1.60	0.62	1.29
20t	128.2	0.780	4322	3125	2648	0.72	0.56	1.29	0.77	1.38
21t	"	"	4340	3213	2881	0.74	0.61	1.22	0.82	1.35
22t	"	"	3294	2394	2012	0.73	0.56	1.30	0.76	1.38
23t	170.9	0.585	626	430	446	0.69	0.65	1.06	0.94	1.46
24t	"	"	832	579	607	0.70	0.67	1.04	0.95	1.44
25t	"	"	826	562	576	0.68	0.64	1.06	0.93	1.47

Table III. 12. Dependence of R on Trans-Dichloroethylene Pressure

Pressure of Propane = 21.4 mm Hg
 Pressure of Trans-Dichloroethylene = variable. Temp. = 79.5°C.
 Pressure of Chlorine = 42.7 mm Hg

Run No.	P_{t-DCE} mm Hg	$1/P_{t-DCE}$ mm Hg ⁻¹ x10 ²	Area n-PrCl	Area c-DCE	Area TCE	c-DCE R n-PrCl	TCE R n-PrCl	c-DCE R TCE	TCE R c-DCE	n-PrCl R c-DCE
26t	5.3	18.7	5411	1193	580	0.88	0.39	2.24	0.44	1.13
27t	"	"	6099	1354	593	0.89	0.36	2.49	0.40	1.12
28t	"	"	5193	1094	542	0.85	0.38	2.20	0.45	1.19
29t	10.7	9.36	2944	1281	651	0.87	0.40	2.15	0.46	1.15
30t	"	"	3766	1575	851	0.84	0.41	2.02	0.49	1.20
31t	"	"	2713	1149	556	0.86	0.38	2.07	0.44	1.18
7t	21.4	4.67	2412	2117	1181	0.88	0.45	1.96	0.51	1.14
8t	"	"	3130	2542	1428	0.81	0.42	1.94	0.51	1.23
9t	"	"	2898	2453	1332	0.85	0.42	2.06	0.49	1.18
32t	42.7	2.34	1966	3138	1928	0.80	0.45	1.77	0.56	1.25
33t	"	"	1240	1931	1223	0.78	0.45	1.72	0.58	1.28
34t	"	"	1073	1779	1167	0.80	0.50	1.66	0.60	1.21
+ 35t	85.5	1.17	163	491	416	0.75	0.58	1.29	0.77	1.33
+ 36t	"	"	229	695	584	0.76	0.59	1.30	0.76	1.32
+ 37t	"	"	702	2011	1726	0.72	0.56	1.27	0.78	1.39

+ Part of reaction mixture analysed.

Table III. 13. Dependence of R on Propane Pressure

Pressure of Propane = variable
 Pressure of Trans-Dichloroethylene = 21.4 mm Hg Temp. = 79.5°C
 Pressure of Chlorine = 42.7 mm Hg

Run No.	P PrH mm Hg	$\frac{1}{P} P_{PrH}$ mm Hg ⁻¹ x10 ²	Area n-PrCl	Area c-DCE	Area TCE	c-DCE R n-PrCl	TCE R n-PrCl	c-DCE R TCE	TCE R c-DCE	n-PrCl R c-DCE
38t	5.3	18.7	569	1956	901	0.86	0.36	2.37	0.42	1.16
39t	"	"	580	2099	925	0.90	0.38	2.35	0.40	1.11
40t	"	"	614	2085	1006	0.85	0.37	2.26	0.44	1.18
41t	10.7	9.36	1135	1985	911	0.87	0.37	2.37	0.42	1.15
42t	"	"	1036	1853	888	0.89	0.39	2.27	0.44	1.12
43t	"	"	752	1318	710	0.88	0.43	2.02	0.49	1.14
7t	21.4	4.67	2412	2117	1181	0.88	0.45	1.96	0.51	1.14
8t	"	"	3130	2542	1428	0.81	0.42	1.94	0.51	1.23
9t	"	"	2898	2453	1332	0.85	0.42	2.06	0.49	1.18
44t	42.7	2.34	4280	1690	1055	0.80	0.48	1.65	0.57	1.27
45t	"	"	4330	1680	962	0.78	0.43	1.80	0.52	1.29
46t	"	"	4196	1661	1064	0.79	0.47	1.70	0.58	1.26
47t	85.5	1.17	4842	888	634	0.74	0.48	1.53	0.65	1.36
48t	"	"	4539	870	675	0.77	0.55	1.41	0.71	1.30
49t	"	"	5157	925	751	0.72	0.53	1.34	0.74	1.39

Table III. 14. Dependence of R on Chlorine Pressure

Pressure of Propane = 21.4 mm Hg
 Pressure of Trans-Dichloroethylene = 21.4 mm Hg Temp. = 79.5°C.
 Pressure of Chlorine = variable

Run No.	P _{Cl₂} mm Hg	¹ /P _{Cl₂} mm Hg ⁻¹ x10 ²	Area n-PrCl	Area c-DCE	Area TCE	c-DCE R n-PrCl	TCE R n-PrCl	c-DCE R TCE	TCE R c-DCE	n-PrCl R c-DCE
56t	21.3	4.70	1049	926	431	0.88	0.38	2.34	0.42	1.13
57t	"	"	973	899	430	0.92	0.40	2.28	0.44	1.08
58t	"	"	644	585	251	0.91	0.36	2.54	0.39	1.10
59t	"	"	1170	1058	462	0.90	0.36	2.50	0.40	1.11
7t	42.7	2.34	2412	2117	1181	0.88	0.45	1.96	0.51	1.14
8t	"	"	3130	2542	1428	0.81	0.42	1.94	0.51	1.23
9t	"	"	2898	2453	1332	0.85	0.42	2.06	0.49	1.18
60t	87.4	1.14	4777	3887	2705	0.81	0.52	1.57	0.63	1.23
61t	"	"	4569	3587	2455	0.78	0.49	1.59	0.62	1.27
62t	"	"	4205	3283	2223	0.78	0.48	1.61	0.62	1.28
63t	"	"	4605	3594	2520	0.78	0.50	1.55	0.64	1.28
64t	130	0.77	5344	3795	3274	0.71	0.56	1.27	0.79	1.41
65t	"	"	4907	3326	3336	0.68	0.62	1.10	0.91	1.48
66t	"	"	5364	3812	3635	0.71	0.62	1.14	0.87	1.41
67t	171	0.585	4185	2604	3230	0.62	0.71	0.88	1.13	1.61
68t	"	"	3362	2146	2631	0.64	0.72	0.89	1.12	1.56
69t	"	"	2751	1743	2260	0.63	0.75	0.84	1.18	1.58
70t	212	0.473	5726	3406	5065	0.59	0.81	0.73	1.35	1.68
71t	"	"	5342	3169	4909	0.59	0.84	0.70	1.41	1.68
72t	"	"	3065	1603	2601	0.53	0.78	0.67	1.48	1.91
73t	278 ²⁰⁷	0.360	5479	2855	5189	0.52	0.87	0.60	1.65	1.92
74t	"	"	5528	2895	5260	0.52	0.87	0.60	1.65	1.91
75t	"	"	5830	3117	5656	0.53	0.89	0.60	1.65	1.87
76t	343	0.292	1655	757	1779	0.46	0.98	0.47	2.14	2.18
77t	"	"	1863	973	1923	0.52	0.94	0.55	1.80	1.91
78t	"	"	2833	1289	2878	0.46	0.93	0.49	2.03	2.19

Table III. 15. Dependence of R on Carbon Dioxide Pressure

Pressure of Propane = 21.4 mm Hg
 Pressure of Trans-Dichloroethylene = 21.4 mm Hg
 Pressure of Chlorine = 42.7 mm Hg
 Pressure of Carbon Dioxide = variable

Temp. = 79.5°C.

Run No.	P _{CO2} mm Hg	1/P _{CO2} mm Hg ⁻¹ x10 ²	Area n-PrCl	Area c-DCE	Area TCE	c-DCE R n-PrCl	TCE R n-PrCl	c-DCE R TCE	TCE R c-DCE	n-PrCl R c-DCE
7t	0	—	2412	2117	1181	0.88	0.45	1.96	0.51	1.14
8t	"	—	3130	2542	1428	0.81	0.42	1.94	0.51	1.23
9t	"	—	2898	2453	1332	0.85	0.42	2.06	0.49	1.18
79t	42.7	2.34	5100	4117	2412	0.81	0.43	1.86	0.53	1.24
80t	"	"	2288	1868	1180	0.82	0.47	1.73	0.57	1.22
81t	"	"	2940	2226	1406	0.76	0.44	1.73	0.57	1.32
82t	85.5	1.17	2716	2043	1624	0.75	0.55	1.37	0.72	1.33
83t	"	"	4416	3338	2650	0.76	0.55	1.37	0.72	1.32
84t	"	"	2494	1822	1291	0.73	0.48	1.54	0.65	1.37
85t	128	0.78	2315	1616	1516	0.70	0.60	1.16	0.85	1.43
86t	"	"	2388	1651	1597	0.69	0.61	1.12	0.88	1.45
87t	"	"	2131	1510	1489	0.71	0.64	1.10	0.90	1.41
88t	171	0.585	3462	2206	2511	0.64	0.66	0.96	1.04	1.57
89t	"	"	3092	1954	2098	0.63	0.62	1.02	0.98	1.58
90t	"	"	2573	1668	1864	0.65	0.66	0.98	1.02	1.54
91t	235	0.426	3174	1957	2306	0.62	0.67	0.93	1.07	1.62
92t	"	"	2055	1346	1539	0.65	0.69	0.95	1.04	1.53
93t	"	"	880	599	652	0.68	0.68	1.00	1.00	1.47
94t	299	0.334	2677	1532	2155	0.57	0.74	0.77	1.28	1.75
95t	"	"	2328	1356	1835	0.58	0.72	0.81	1.23	1.72
96t	"	"	2042	1258	1622	0.62	0.73	0.85	1.17	1.62

1. The Dark Reaction

In the chlorination of ethylene Hagopian^{51,52} found an appreciable dark formation of dichloroethane which he attributed to a molecular association on the surface. With propene and isobutene the rate of the dark reaction was much greater. In their study of the chlorination of the chloroethylenes, however, Dainton and co-workers^{46,63,75,79} found that the dark reaction was negligibly small.

In order to check that surface formation of tetrachloroethane was unimportant in our system experiments were carried out in which the reaction mixture was allowed to stand in the dark for 30 minutes, instead of the usual two, before illumination. The results are recorded in tables III.1 and III.9 and it will be seen that, within experimental error, R is independent of the length of the pre-illumination dark time and it was concluded that the dark reaction was unimportant. This was confirmed by other experiments in which the mixture was left in the dark for 2-5 minutes and then submitted to the usual inhibition and analysis procedure, the amounts of product obtained being immeasurably small apart from 1,2 dichloropropane, presumably formed by the rapid surface addition of chlorine to the small amount of propylene present as impurity in the propane: although the formation of 1,2 dichloropropane was not investigated in detail it was always produced in amounts which depended on the pressure of propane in the mixture but was independent of the length of dark time, the period of illumination and the extent of the reaction. This would appear to confirm Hagopian's view that the dark addition of chlorine to propylene is very rapid.

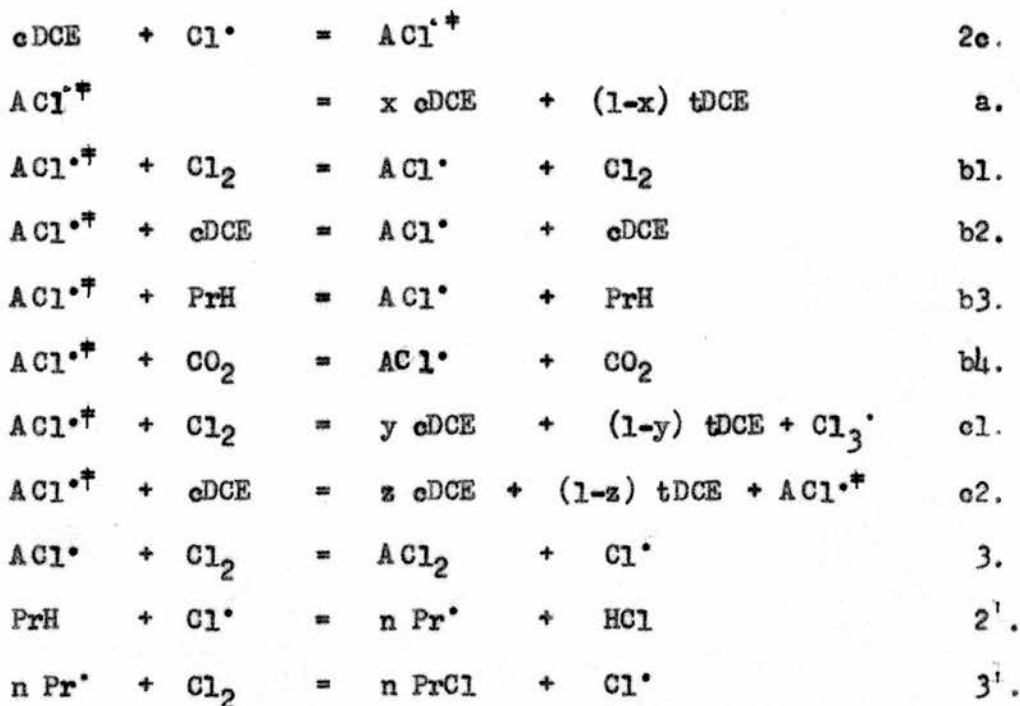
2. The reaction Mechanism

From the results in tables and figures III.2 - III.7 and III.10 - III.15 it can be seen that $R_{n \text{ PrCl}}^{\text{TCE}}$ increases with increasing pressure and that there is a corresponding decrease in $R_{n \text{ PrCl}}^{\text{1DCE}}$. Varying the ratio of propane to dichloroethylene has no marked effect. It is noteworthy that increasing the pressure of an inert gas (carbon dioxide) has a similar effect to increasing the pressure of the reactants.

Taking up the suggestion of Ayscough, Cocker and Dainton⁴⁶ that the radical formed by the addition of a chlorine atom to an olefine must initially contain energy in excess of that of the same radical in its ground state by an amount equal to the activation energy (E_2) plus the heat of the reaction (ΔH_2) it is necessary to consider the following reactions which the energetic radical (ACl^*) can undergo:

- (a) The transition state for the formation of the radical is also the transition state for its decomposition and since the hot radical possesses energy equal to that of the transition state it can spontaneously decompose into a chlorine atom and either cis or trans dichloroethylene.
- (b) The radical may lose its excess energy by collision with other molecules in the system.
- (c) The radical may be involved in an atom exchange reaction with either a chlorine or a dichloroethylene molecule.

Those reactions are included in the following scheme for the competitive chlorination of cis dichloroethylene and propane (the reactions involved in the formation of iso propyl chloride can be neglected since the relative rate of abstraction of primary and secondary hydrogen from propane by a chlorine atom depends only on temperature⁴⁹). An identical scheme can be applied to the trans dichloroethylene/propane system.



from this mechanism it follows that:

$$\frac{R_{\text{TCE}}}{n R_{\text{PrCl}}} = \frac{k_{2c}}{k_2'} \frac{(k_{b1} [\text{Cl}_2] + k_{b2} [\text{cDCE}] + k_{b3} [\text{PrH}] + k_{b4} [\text{CO}_2])}{(k_a + (k_{b1} + k_{c1}) [\text{Cl}_2] + (k_{b2} + k_{c2}) [\text{cDCE}] + k_{b3} [\text{PrH}] + k_{b4} [\text{CO}_2])} \quad \text{III.1.}$$

$$\frac{R_{\text{tDCE}}}{n R_{\text{PrCl}}} = \frac{k_{2c}}{k_2'} \frac{((1-x) k_a + (1-y) k_{c1} [\text{Cl}_2] + (1-z) k_{c2} [\text{cDCE}])}{(k_a + (k_{b1} + k_{c1}) [\text{Cl}_2] + (k_{b2} + k_{c2}) [\text{cDCE}] + k_{b3} [\text{PrH}] + k_{b4} [\text{CO}_2])} \quad \text{III.2}$$

$$\frac{R_{\text{tDCE}}}{R_{\text{TCE}}} = \frac{((1-x) k_a + (1-y) k_{c1} [\text{Cl}_2] + (1-z) k_{c2} [\text{cDCE}])}{(k_{b1} [\text{Cl}_2] + k_{b2} [\text{cDCE}] + k_{b3} [\text{PrH}] + k_{b4} [\text{CO}_2])} \quad \text{III.3}$$

At very high pressures of chlorine equation III.3 reduces to

$$\frac{R_{\text{tDCE}}}{R_{\text{TCE}}} = \frac{(1-y) k_{c1}}{k_{b1}} \quad \text{III.4}$$

The corresponding equation for the trans dichloroethylene/propane system is

$$\frac{R_{\text{cDCE}}}{R_{\text{TCE}}} = \frac{y k_{c1}}{k_{b1}} \quad \text{III.5}$$

The graphs obtained by plotting R_{TCE}^{IDCE} against the reciprocal of chlorine pressure should, therefore, have intercepts at $1/P_{Cl_2} = 0$ of $(1-y)k_{c1}/k_{b1}$ and yk_{c1}/k_{b1} , respectively. Examination of figs. III.6a and III.14a shows that the intercepts are certainly small and probably zero and this can be interpreted to mean that reaction c1 does not occur (i.e. $(1-y)k_{c1}Cl_2 = yk_{c1}Cl_2 = 0$). *↳ significantly in relation to reaction b1.*

Similarly if the atom exchange reaction c2 occurs graphs of R_{TCE}^{IDCE} against the reciprocal of olefine pressure should have intercepts of $(1-z)k_{c2}/k_{b2}$ and zk_{c2}/k_{b2} , respectively. It was not possible to work at pressures of olefine high enough to obtain a conclusive indication of what the intercepts would be but the graphs are similar to those for lower pressures of chlorine and also to those for propane and carbon dioxide with which atom transfer reactions cannot occur and it was therefore concluded that reaction c2 is unimportant. (Figs. III.8a and III.16a - note that average points have been plotted). The individual graphs are, of course, not parallel because of the effect of the other components of the reaction mixture and their different efficiencies in collisional deactivation. From the graphs of R_{TCE}^{IDCE} v. $1/P_{Mix}$. it is obvious that the intercept must be small, confirming conclusion that atom exchange between the radical and the olefine is unimportant.

Neglecting reactions c1 and c2 equations III.1 - III.3 reduce to

$$R_{n PrCl}^{TCE} = \frac{k_{2c} (k_{b1} [Cl_2] + k_{b2} [cDCE] + k_{b3} [PrH] + k_{b4} [CO_2])}{k_2' (k_a + k_{b1} [Cl_2] + k_{b2} [cDCE] + k_{b3} [PrH] + k_{b4} [CO_2])} \quad \text{III.6}$$

$$R_{cDCE}^{n PrCl} = \frac{k_2' (k_a + k_{b1} [Cl_2] + k_{b2} [cDCE] + k_{b3} [PrH] + k_{b4} [CO_2])}{k_{2c} (1-x) k_a} \quad \text{III.7}$$

$$R_{cDCE}^{TCE} = \frac{(k_{b1} [Cl_2] + k_{b2} [cDCE] + k_{b3} [PrH] + k_{b4} [CO_2])}{(1-x) k_a} \quad \text{III.8}$$

The corresponding equations for the trans dichloroethylene/propane system are:

$$R_{n \text{ PrCl}}^{\text{TCE}} = \frac{k_2' (k_{b1} [\text{Cl}_2] + k_{b2} [\text{tDCE}] + k_{b3} [\text{PrH}] + k_{b4} [\text{CO}_2])}{k_{2t} (k_a + k_{b1} [\text{Cl}_2] + k_{b2} [\text{tDCE}] + k_{b3} [\text{PrH}] + k_{b4} [\text{CO}_2])} \quad \text{III.9}$$

$$R_{\text{cDCE}}^{n \text{ PrCl}} = \frac{k_2' (k_a + k_{b1} [\text{Cl}_2] + k_{b2} [\text{tDCE}] + k_{b3} [\text{PrH}] + k_{b4} [\text{CO}_2])}{k_{2t} \times k_a} \quad \text{III.10}$$

$$R_{\text{cDCE}}^{\text{TCE}} = \frac{(k_{b1} [\text{Cl}_2] + k_{b2} [\text{tDCE}] + k_{b3} [\text{PrH}] + k_{b4} [\text{CO}_2])}{x k_a} \quad \text{III.11}$$

In agreement with equations III.7, III.8, III.10 and III.11 the graphs of $R_{\text{tDCE}}^{n \text{ PrCl}}$, $R_{\text{tDCE}}^{\text{TCE}}$, $R_{\text{cDCE}}^{n \text{ PrCl}}$ and $R_{\text{cDCE}}^{\text{TCE}}$ against reactant and inert gas pressure (figs. III.3b - III.7b and III.11b - III.15b) are straight lines within the limits of experimental error and the gradients of the lines

$$- \frac{k_2' k_b}{k_{2c}(1-x)k_a}, \quad \frac{k_b}{(1-x)k_a}, \quad \frac{k_2' k_b}{k_{2t} x k_a} \quad \text{and} \quad \frac{k_b}{x k_a} -$$

are recorded in Table III.17 (page 83) together with the derived values of k_{2c}/k_2' , k_{2t}/k_2' and $x/(1-x)$.

The latter values were also obtained by the following alternative method: the relative rate of reactions 2c and 2' is given by:

$$\frac{d [\text{ACl} \cdot^*]}{dt} / \frac{d [n \text{ Pr} \cdot]}{dt} = \frac{k_{2c} [\text{cDCE}] [\text{Cl} \cdot]}{k_2' [\text{PrH}] [\text{Cl} \cdot]} \quad \text{III.12}$$

Assuming that the chains are long, all the n propyl radicals are converted to n propyl chloride but the energetic trichloroethyl radicals have two possible fates:

- a) collisional deactivation and subsequent reaction with chlorine to form tetrachloroethane, or
- b) spontaneous decomposition to form cis and trans dichloroethylene in the ratio $x : (1-x)$ and to obtain the total amount of decomposition it is, therefore, necessary to divide the measured amount of trans dichloroethylene formed by $(1-x)$.

$$\text{From III.12} \quad \frac{k_{2c}}{k_2'} = \frac{d[ACl^{\bullet\ddagger}]}{[cDCE]} \bigg/ \frac{d[nPr^{\bullet}]}{[PrH]} = R_{nPrCl}^{\text{total}}$$

where "total" represents the total fate of $ACl^{\bullet\ddagger}$

$$\therefore \frac{k_{2c}}{k_2'} = n_c R_{nPrCl}^{\text{t DCE}} + R_{nPrCl}^{\text{TCE}} \quad \text{III.13}$$

$$\text{where } n_c = \frac{1}{(1-x)}$$

$$\text{Similarly} \quad \frac{k_{2t}}{k_2'} = n_t R_{nPrCl}^{\text{c DCE}} + R_{nPrCl}^{\text{TCE}} \quad \text{III.14}$$

$$\text{where } n_t = \frac{1}{x}$$

n_c and n_t and k_{2c}/k_2' and k_{2t}/k_2' were evaluated from the gradients and intercepts respectively of the corresponding graphs (figs. III.3c - III.8c and III.11c - III.16c) using the method of least squares and are given in table III.18 (page 83) - the errors quoted are twice the standard deviation.

Table III.17. Rate Constants derived from graphs of R_{1-DCE}^{n-PrCl} and R_{1-DCE}^{TCE} against pressure (Temp. = 79.5°C.)

Variable Pressure	mm Hg ⁻¹ x 10 ³					
	$\frac{k_2'k_b}{k_2(1-x)k_a}$	k_b	$\frac{k_2'k_b}{k_2xk_a}$	$\frac{k_b}{xk_a}$	$\frac{x}{1-x}$	$\frac{k_2t}{k_2'}$
PrH+DCE	7.23	14.1	2.65	4.12	3.4	1.55
DCE	5.23	12.0	2.56	4.11	2.9	1.60
PrH	5.56	12.0	2.61	3.69	3.2	1.42
Cl ₂	5.88	14.2	3.16	4.89	2.9	1.54
CO ₂	3.13	6.77	1.67	2.47	2.7	1.48

Table III.18. Rate Constants derived from graphs of R_{n-PrCl}^{TCE} v. R_{n-PrCl}^{iDCE} (Temp. 79.5°C)

Variable Pressure	n_c	n_t	$1-x$	x	$\frac{x}{1-x}$	$\frac{k_2c}{k_2'}$	$\frac{k_2t}{k_2'}$
DCE	-4.46 [±] 1.06	-1.23 [±] 0.28	0.23 [±] 0.07	0.81 [±] 0.25	3.6	2.09 [±] 0.33	1.46 [±] 0.23
PrH	-3.54 [±] 0.86	-1.16 [±] 0.32	0.28 [±] 0.09	0.86 [±] 0.33	3.1	1.80 [±] 0.27	1.40 [±] 0.30
Cl ₂	-5.39 [±] 0.38	-1.34 [±] 0.19	0.19 [±] 0.01	0.75 [±] 0.05	4.0	2.43 [±] 0.10	1.57 [±] 0.06
CO ₂	-4.10 [±] 0.58	-1.16 [±] 0.14	0.24 [±] 0.04	0.86 [±] 0.14	3.5	2.00 [±] 0.16	1.40 [±] 0.10
Total Results	-4.75 [±] 0.26	-1.30 [±] 0.06	0.21 [±] 0.02	0.77 [±] 0.04	3.7	2.20 [±] 0.08	1.52 [±] 0.08

If the proposed mechanism is valid k_{2c}/k_2' and k_{2t}/k_2' should be independent of the method of evaluation and it can be seen from table III.18 that for trans dichloroethylene the rate constant ratios obtained from the individual sets of results for each component of the reaction mixture are, within the limits of error, identical with that obtained by combining all the results for this system and that the values given in table III.17 are in good agreement. For cis dichloroethylene the experimental error is greater and the agreement is less satisfactory: in particular the value of k_{2c}/k_2' with chlorine as the variable pressure appears to be high (see also fig.III.8c). One possible explanation of this is that at high pressures of chlorine there is some surface formation of tetrachloroethane: the original checks for surface reaction were carried out using a reaction mixture of 32.1 mm each of propane and dichloroethylene and 42.7 mm of chlorine.

From table III.18 the best value of $x/(1-x)$ is about 3.6 whereas that obtained from table III.17 is about 3.0. The former were derived from n_c and n_t , the gradients of the $R_n^{tDCE} \text{ v. } R_n^{TCE}$ and $R_n^{cDCE} \text{ v. } R_n^{TCE}$ graphs and the fact that $(\frac{1}{n_c} + \frac{1}{n_t})$ can reasonably be taken as being equal to one suggests that x is the same for the radicals formed from cis and trans dichloroethylene. If k_b is the collision number and is independent of the nature of the complex the lower value of 3.0, obtained from $\frac{k_b}{(1-x)k_a} / \frac{k_b}{xk_a}$ may be due to a different value of k_a for the two radicals, suggesting that they differ in energy. If those assumptions are valid then

$$\begin{aligned} \frac{x}{(1-x)} \frac{k_{at}}{k_{ac}} &= 3.0 \\ &= 3.6 \frac{k_{at}}{k_{ac}} \end{aligned}$$

$$\therefore k_{at} \sim 0.85 k_{ac}$$

Taking 3.6 as the real value of $x/(1-x)$ the radical ACl^{\bullet} decomposes as follows:

$$\sum ACl^{\bullet} \sum \underline{k_a} \quad 0.78 \text{ oDCE} + 0.22 \text{ tDCE}$$

The relative value of k_b for the various components of the reaction mixture can be estimated from the complex rate constants in table III.17 to be

	Cl ₂	oDCE	tDCE	PrH	CO ₂
k_b	1.0	0.8	0.8	0.8	0.5

k_b for chlorine can be calculated from the standard collision number (Z) for chlorine and trichloroethyl radicals, assuming that deactivation occurs on every collision. The collision diameters used for chlorine and the trichloroethyl radical are given in the following table together with those for the other components of the reaction mixture and the values of k_b calculated from k_b for chlorine and the relative values of k_b given above. (The collision diameters for chlorine and carbon dioxide are those quoted by Glasstone and Lewis⁹⁷ and that for propane by Reid and Sherwood⁹⁸. The relationship

$$\sigma = 0.833 V_c^{1/3}$$

, where σ is the collision diameter and V_c the critical volume, which the latter authors give was used to calculate the collision diameters for dichloroethylene and the trichloroethyl radical; the critical volume for the trichloroethyl radical was taken as being equal to that for trichloroethane).

	Cl ₂	CO ₂	PrH	o-DCE	t-DCE	C ₂ H ₂ Cl ₃
	4.5	4.2	5.01	5.0	5.0	5.5
$k_b \times 10^{-7} \text{ sec}^{-1}$	8.65	4	7	7	7	-

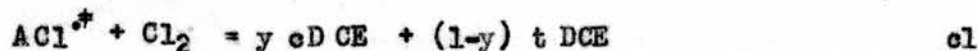
It follows that the other molecules require about twice as many collisions as chlorine to deactivate the hot radical.

3. The Arrhenius Parameters

In order to determine the Arrhenius parameters for reactions 2c and 2t and to investigate any variation of x and k_a with temperature similar series of experiments were carried out at 35°C and 132.5°C. Pressure of chlorine was chosen as the variable in those experiments since this allowed the largest possible range of values to be investigated: the pressure of olefine that could be used was limited by its low saturated vapour pressure (16 cm at 20°C for cis dichloroethylene); the use of a large pressure of propane would have increased the analytical difficulties as a result of high propane/dichloroethylene ratios and carbon dioxide suffers from the disadvantage of being much less efficient than chlorine in collisional deactivation of the hot radical.

The results discussed in the last section suggest that there may be some surface reaction with cis dichloroethylene at high chlorine pressures and the values of A_{2c}/A_2' should be regarded as a maximum. Since the importance of reactions occurring on the surface would be expected to decrease with increasing temperature, $-(E_{2c} - E_2')$ also represents an upper limit and hence E_{2c} must be taken as a minimum value.

The experimental results are presented in tables III.19 - III.22 and figs. III.19, a,b,c - III.22, a,b,c. The general behaviour is similar to that found at 79.5°C and the fact that the plots of R_{TCE}^{1DCE} against the reciprocal of chlorine pressure (figs. III.19a - III.22a) all go through the origin is further confirmation that the reaction



does not occur.

The rate constants were calculated from those graphs as before and

are given in table III.23. It may be noted that the value obtained for x is in reasonable agreement with the 0.78 deduced from the experiments at 79.5°C: at 132.5°C, however, $x/(1-x)$, calculated from $\frac{k_b}{(1-x)k_a} / \frac{k_D}{xk_a}$, is 3.8 (in comparison with ~ 3.0 at 79.5°C) which suggests that at this temperature k_a is nearly the same for the two radicals formed from cis and trans dichloroethylene. As before k_b was calculated from the standard collision number and the values of k_a thus derived.

The Arrhenius plots for k_{2c}/k_2' and k_{2t}/k_2' are shown in fig. III.23 and for k_{ac} and k_{at} in fig. III.24. The derived activation energies and A factors are:-

From fig. III.23

$$\frac{A_{2c}}{A_2'} = 0.78 \pm 0.09, \quad \frac{A_{2t}}{A_2'} = 0.29 \pm 0.02$$

$$(E_{2c} - E_2') = -790 \pm 120 \text{ cal.mole}^{-1}, \quad (E_{2t} - E_2') = -1150 \pm 100 \text{ cal.mole}^{-1}.$$

As stated in the introduction, the following values for E_2' and A_2' were used as standard³⁴:

$$A_2' = 1.7 \pm 0.3 \times 10^{10} \text{ l.mole}^{-1} \text{ sec}^{-1} \text{ per H atom}$$

$$E_2' = 980 \pm 130 \text{ cal.mole}^{-1}.$$

Hence

$$A_{2c} = 8.0 \pm 2.2 \times 10^{10} \text{ l.mole}^{-1} \text{ sec}^{-1}$$

$$A_{2t} = 3.0 \pm 0.7 \times 10^{10} \text{ l.mole}^{-1} \text{ sec}^{-1}$$

$$E_{2c} = 190 \pm 250 \text{ cal.mole}^{-1}$$

$$E_{2t} = -170 \pm 230 \text{ cal.mole}^{-1}$$

From fig. III.24

$$A_{ac} = A_{at} = 1.8 \pm 0.5 \times 10^{10} \text{ sec}^{-1}$$

$$E_{ac} = 1280 \pm 200 \text{ cal.mole}^{-1}$$

$$E_{at} = 1380 \pm 200 \text{ cal.mole}^{-1}$$

Note that the error limits were derived from the reasonable maximum and minimum gradients of the graphs.

Table III. 19. Dependence of R on Chlorine Pressure

Pressure of Propane = 21.4 mm Hg
 Pressure of Cis-Dichloroethylene = 21.4 mm Hg Temp. = 35°C.
 Pressure of Chlorine = variable

Run No.	P _{Cl₂} mm Hg	1/P _{Cl₂} mm Hg ⁻¹ x10 ²	Area n-PrCl	Area t-DCE	Area TCE	t-DCE R n-PrCl	TCE R n-PrCl	t-DCE R TCE	TCE R t-DCE	n-PrCl R t-DCE
109c	21.8	4.59	1054	469	1058	0.445	0.92	0.483	2.05	2.24
110c	"	"	1214	491	1167	0.404	0.88	0.459	2.25	2.47
111c	"	"	1184	520	1209	0.439	0.93	0.469	2.12	2.28
112c	42.9	2.33	1059	403	1158	0.381	1.00	0.380	2.61	2.63
113c	"	"	1793	721	2109	0.402	1.08	0.376	2.66	2.49
114c	"	"	1799	705	2100	0.392	1.07	0.366	2.71	2.55
115c	86.2	1.16	2150	786	2812	0.365	1.20	0.305	3.25	2.74
116c	"	"	2302	831	2837	0.361	1.13	0.319	3.11	2.77
117c	"	"	2756	944	3572	0.343	1.19	0.288	3.45	2.92
118c	129.5	0.772	2151	694	3003	0.323	1.28	0.252	3.94	3.10
119c	"	"	2090	680	2814	0.325	1.23	0.264	3.77	3.07
120c	"	"	1975	684	2833	0.346	1.31	0.263	3.78	2.89
121c	173	0.578	1935	602	2998	0.311	1.42	0.219	4.53	3.21
122c	"	"	1714	524	2722	0.306	1.45	0.210	4.73	3.27
123c	"	"	1859	557	3001	0.300	1.48	0.202	4.90	3.34
124c	214	0.467	2340	631	4218	0.270	1.65	0.163	6.1	3.71
125c	"	"	2053	603	3597	0.294	1.60	0.183	5.45	3.40
126c	279	0.358	3463	879	6603	0.254	1.75	0.146	6.8	3.94
127c	"	"	2309	531	4202	0.230	1.66	0.138	7.9	4.35
128c	"	"	2294	535	4230	0.233	1.69	0.138	7.2	4.28
129c	342	0.292	3102	636	6590	0.205	1.92	0.107	9.4	4.87
130c	"	"	3462	697	6828	0.201	1.80	0.111	8.9	4.96
131c	"	"	3014	605	6095	0.201	1.85	0.110	9.2	4.98

Table III. 20. Dependence of R on Chlorine Pressure

Pressure of Propane = 21.4 mm Hg
 Pressure of Cis-Dichloroethylene = 21.4 mm Hg Temp. = 132.5°C.
 Pressure of Chlorine = variable

Run No.	P _{Cl₂} mm Hg	$\frac{1}{P_{Cl_2}}$ mm Hg ⁻¹ x10 ²	Area n-PrCl	Area t-DCE	Area TCE	t-DCE R n-PrCl	TCE R n-PrCl	t-DCE R TCE	TCE R t-DCE	n-PrCl R t-DCE
132c	21.4	4.67	849	325	147	0.383	0.158	2.41	0.41	2.61
133c	"	"	1657	630	293	0.385	0.162	2.38	0.42	2.63
134c	"	"	843	328	158	0.389	0.171	2.26	0.44	2.57
135c	43.3	2.31	1414	533	341	0.377	0.221	1.74	0.58	2.65
136c	"	"	1573	579	417	0.368	0.243	1.52	0.65	2.72
137c	"	"	1366	517	367	0.379	0.246	1.54	0.65	2.64
138c	"	"	1776	633	424	0.357	0.219	1.63	0.61	2.80
139c	64.6	1.55	2916	1023	989	0.351	0.311	1.18	0.88	2.85
140c	"	"	4112	1389	1469	0.338	0.327	1.03	0.96	2.96
141c	86.1	1.16	1104	363	457	0.329	0.379	0.86	1.15	3.04
142c	"	"	1277	420	605	0.329	0.433	0.76	1.31	3.04
143c	"	"	1217	404	544	0.332	0.409	0.81	1.23	3.01
144c	127	0.79	2061	645	1190	0.313	0.528	0.591	1.68	3.20
145c	"	"	2945	934	1693	0.317	0.526	0.602	1.65	3.15
146c	"	"	2786	859	1400	0.308	0.460	0.614	1.63	3.24
147c	171	0.585	1791	496	1279	0.277	0.653	0.423	2.35	3.61
148c	"	"	6841	1964	4747	0.287	0.634	0.451	2.20	3.48
149c	"	"	4654	1377	3293	0.295	0.647	0.455	2.17	3.38
150c	214	0.468	4132	1110	3531	0.269	0.782	0.343	2.89	3.72
151c	"	"	4042	1052	3276	0.260	0.747	0.350	2.83	3.84
152c	"	"	4273	1142	3516	0.267	0.753	0.354	2.80	3.74

Table III. 21. Dependence of R on Chlorine Pressure

Pressure of Propane = 21.4 mm Hg
 Pressure of Trans-Dichloroethylene = 21.4 mm Hg Temp. = 35°C.
 Pressure of Chlorine = variable

Run No.	P _{Cl₂} mm Hg	$\frac{1}{P_{Cl_2}}$ mm Hg ⁻¹ x10 ²	Area n-PrCl	Area c-DCE	Area TCE	c-DCE R n-PrCl	TCE R n-PrCl	c-DCE R TCE	TCE R c-DCE	n-PrCl R c-DCE
101t	21.5	4.66	1380	1409	827	1.02	0.55	1.86	0.54	0.98
102t	"	"	1163	1333	702	1.15	0.55	2.07	0.48	0.87
103t	"	"	1401	1577	769	1.12	0.50	2.23	0.44	0.89
104t	42.7	2.34	1849	1716	1303	0.93	0.64	1.43	0.69	1.08
105t	"	"	1878	2032	1425	1.08	0.69	1.56	0.64	0.92
106t	"	"	2046	2078	1364	1.02	0.61	1.66	0.60	0.98
107t	"	"	2027	2037	1383	1.01	0.63	1.60	0.62	0.99
108t	85.6	1.17	1112	1000	968	0.90	0.80	1.13	0.88	1.11
109t	"	"	672	610	588	0.90	0.80	1.13	0.88	1.10
110t	128	0.78	1830	1499	1913	0.82	0.96	0.85	1.16	1.22
111t	"	"	2202	1779	2198	0.81	0.91	0.88	1.12	1.24
112t	"	"	2532	1832	2580	0.72	0.93	0.78	1.28	1.38
113t	171	0.585	2496	1830	2713	0.73	1.00	0.74	1.35	1.36
114t	"	"	1468	1022	1747	0.70	1.09	0.64	1.55	1.44
115t	"	"	2247	1512	2542	0.67	1.03	0.65	1.53	1.49
116t	214	0.468	2722	1713	3153	0.63	1.06	0.59	1.67	1.59
117t	"	"	2528	1616	3116	0.64	1.13	0.57	1.75	1.56
118t	"	"	1107	716	1315	0.65	1.09	0.59	1.67	1.55
119t	278	0.360	2072	1226	2823	0.59	1.25	0.473	2.10	1.69
120t	"	"	3761	2206	4911	0.59	1.19	0.489	2.03	1.70
121t	"	"	2874	1540	3642	0.54	1.16	0.461	2.15	1.87
122t	342	0.293	7218	3893	10,020	0.54	1.29	0.416	2.34	1.85
123t	"	"	1271	638	1860	0.50	1.34	0.374	2.65	1.99
124t	"	"	1824	901	2857	0.49	1.43	0.316	2.88	2.02

Table III. 22. Dependence of R on Chlorine Pressure

Pressure of Propane = 21.4 mm Hg
 Pressure of Trans-Dichloroethylene = 21.4 mm Hg Temp. = 132.5°C
 Pressure of Chlorine = variable

Run No.	P _{Cl₂} mm Hg	$\frac{1}{P_{Cl_2}}$ mm Hg ⁻¹ x10 ²	Area n-PrCl	Area c-DCE	Area TCE	c-DCE R n-PrCl	TCE R n-PrCl	c-DCE R TCE	TCE R c-DCE	n-PrCl R c-DCE
125t	21.7	4.62	2160	1834	258	0.85	0.109	7.75	0.128	1.18
126t	"	"	1816	1514	210	0.83	0.106	7.86	0.126	1.20
127t	"	"	1937	1588	209	0.82	0.099	8.29	0.120	1.22
128t	42.9	2.33	4430	3492	682	0.79	0.141	5.59	0.178	1.27
129t	"	"	5811	4691	938	0.81	0.148	5.45	0.182	1.24
130t	"	"	4723	3585	742	0.76	0.144	5.27	0.188	1.32
131t	64.7	1.54	3033	2322	627	0.77	0.189	3.96	0.246	1.30
132t	"	"	1739	1326	409	0.76	0.215	3.53	0.281	1.31
133t	86.1	1.16	7365	5618	1876	0.76	0.233	3.27	0.304	1.31
134t	"	"	5226	3706	1264	0.71	0.222	3.20	0.310	1.41
135t	"	"	4360	3155	1080	0.72	0.227	3.18	0.312	1.38
136t	129	0.77	4341	2962	4176	0.68	0.311	2.19	0.453	1.47
137t	"	"	2922	2020	1008	0.69	0.316	2.19	0.454	1.45
138t	"	"	3151	2178	1089	0.69	0.316	2.18	0.455	1.45
139t	171	0.585	3798	2435	1522	0.64	0.367	1.74	0.569	1.56
140t	"	"	2875	1962	1189	0.68	0.378	1.80	0.551	1.47
141t	"	"	4218	2717	1596	0.64	0.346	1.85	0.535	1.55
142t	214	0.468	2786	1585	1217	0.57	0.399	1.42	0.699	1.76
143t	"	"	2394	1460	1156	0.61	0.440	1.38	0.721	1.64
144t	"	"	2468	1465	1103	0.59	0.410	1.45	0.685	1.68

Table III.23

Pressure of Propane = 21.4 mm Hg.
 Pressure of Cis or Trans Dichloroethylene = 21.4 mm Hg.
 Pressure Chlorine = variable.
 Temp. = variable.

A. Graphs of $R_{n \text{ PrCl}}^{\text{TCE}}$ v. $R_{n \text{ PrCl}}$

Temp. °K	n_c	n_t	$(1-x)$	x	$\frac{x}{(1-x)}$	$\frac{k_{2c}}{k_{2t}}$	$\frac{k_{2t}}{k_{2c}}$
308	-4.26±0.28	-1.28±0.08	0.23±0.02	0.78±0.5	3.4	2.72±0.12	1.94±0.08
352.5	-5.39±0.38	-1.34±0.08	0.19±0.01	0.75±0.5	4.0	2.43±0.10	1.57±0.06
405.5	-4.96±0.30	-1.34±0.12	0.21±0.02	0.75±0.7	3.6	2.06±0.15	1.23±0.09

B. Graphs of $R_{\text{DCE}}^{\text{TCE}}$ v. P_{Cl_2} and $R_{\text{DCE}}^{\text{n PrCl}}$ v. P_{Cl_2}

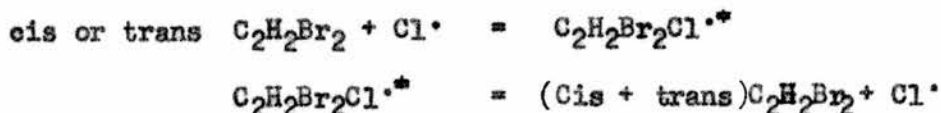
Temp. °K	$\leftarrow \text{mm Hg}^{-1} \times 10^3 \rightarrow$									
	$k_2' k_b$	$\frac{k_b}{k_{2c}(1-x)k_a}$	$\frac{k_b}{k_2 k_a}$	$\frac{k_b}{k_2 x k_a}$	$\frac{k_b}{xk_a}$	$\frac{x}{1-x}$	$\frac{k_{2c}}{k_{2t}}$	$\frac{k_{2t}}{k_{2c}}$	$10^{-7} k_b$ cm Hg ⁻¹ sec ⁻¹	$10^{-9} k_{ac}$ sec ⁻¹
308	7.78	20.8	3.33	6.44	3.2	2.67	1.94	9.3	2.0	1.8
352.5	5.88	14.2	3.16	4.89	2.9	2.42	1.54	8.65	2.7	2.3
405.5	5.87	11.9	2.49	3.12	3.8	2.03	1.25	8.1	3.1	3.3

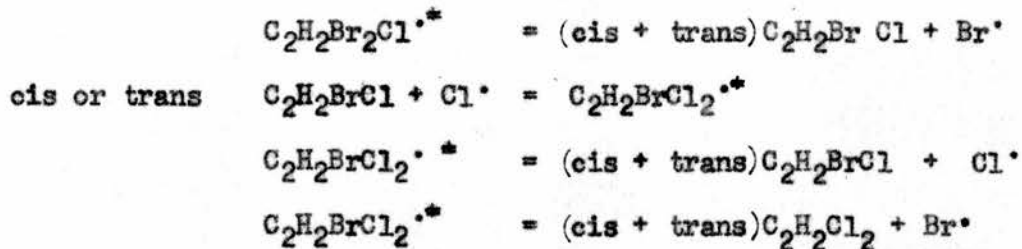
4. Experiments with Cis and Trans Dibromoethylene

Since the dissociation energy of a C — Br bond is less than that of a C — Cl bond it would be expected on the basis of a hot radical mechanism that the addition of a chlorine atom to dibromoethylene would give rise to a radical which could spontaneously decompose to form four products: cis and trans dibromoethylene by the loss of a chlorine atom and cis and trans chlorobromoethylene by loss of a bromine atom. Collisional deactivation of the radical on the other hand should result in the formation of dichloro-dibromoethane.

Experiments were carried out in which mixtures of 5 mm dibromoethylene and < 1 mm chlorine were photolysed for 15 mins; in a number of the experiments a large pressure of carbon dioxide was added to the reaction mixture. The results are given in tables III.25 and III.26.

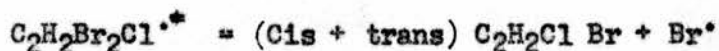
The reaction products were analysed on the same column as was used for the dichloroethylene/propane systems but in this case it was maintained at 51°C for 20 mins. and then heated at 60°/min. At a carrier gas flow rate of 35 ml/min. the retention times for trans and cis dibromoethylene were found to be 18 mins. and 23 mins., respectively, and under the same conditions four other products were detected with retention times of 3 mins.40 secs., 5 mins.55 secs., 7 mins.30 secs. and 13 mins.30 secs. The first two were identified as trans and cis dichloroethylene from the retention times of authentic samples. The remaining two products were not specifically identified but it is not unreasonable to assume that they were trans and cis chlorobromoethylene formed by the following mechanism:





This interpretation is supported by the fact that the dichloroethylenes were not formed in reactions in which the chlorine pressure was low and only a small total amount of reaction occurred. Dichlorodibromoethane, which had a known retention time of 41 mins., was not obtained as a reaction product even in the presence of 400 mm carbon dioxide, but in one experiment (6tb), in which a larger pressure of chlorine was used, a small amount of tetrachloroethane was formed.

Ketelaar et al.⁹⁹ suggested a value of about 13 k.cal.mole⁻¹ for D(C₂H₂Cl₂-Br) and this may be compared with D(C₂H₂Cl₂ - Cl) = 20.3 k.cal. mole⁻¹. It is probable, therefore, that the chlorodibromoethyl radical, formed by the addition of a chlorine atom to dibromoethylene, will initially contain energy in excess of that required to break a C - Br bond by several k.cals. per mole and the unimolecular decomposition:



would be expected to be extremely fast and the probability of collisional deactivation and subsequent formation of C₂H₂Cl₂Br₂ correspondingly small. Similar remarks apply to the C₂H₂BrCl₂^{•*} radical and the production of the dichloroethylenes and tetrachloroethane in this system is understandable.

It is of interest to note that in those experiments in which cis and trans dichloroethylene were produced the amount of cis was about 2.6 times the amount of trans (compare x = 3.6 for the dichloroethylene/propane/chlorine system) and if it is assumed that the chlorobromoethylene isomers are eluted

in the same order as the dibromo and dichloro isomers the ratio of cis to trans is about 1.7. The isomerisation of dibromoethylene could not be directly studied because almost complete isomerisation occurred even in the absence of chlorine.

Table III.25. Chlorination of Cis Dibromoethylene

Pressure of Cis Dibromoethylene ~ 5 mm Hg
 Pressure of Chlorine < 1 mm Hg
 Pressure of Carbon Dioxide = variable
 Temp. = 79.5°C.

Run No.	P _{CO2} mm Hg	Area Ratios ⁺															
		Area t DCE	Area c DCE	Area t CBE	Area c CBE	Area t DBE	Area c DBE	Area t DCE	Area c DCE	Area t DBE	Area c DBE	Area t DCE	Area c CBE				
1cb	nil	-	-	-	-	4001	4895	-	-	-	-	-	-	-	-	-	-
2cb	nil	-	-	-	-	3776	4201	-	-	-	-	-	-	-	-	-	-
3cb	nil	5	12	160	340	3693	4133	.0014	.0033	.0433	.0920	.0017	.0039	.0515	.0937	1.13	2.40
4cb	nil	7	16	209	380	4056	4260	.0017	.0039	.0515	.0937	.0017	.0039	.0515	.0937	1.05	2.29
5cb	nil	73	214	679	1343	3092	4074	.0236	.0695	.220	.434	.0236	.0695	.220	.434	1.32	2.93
6cb	400	48	126	488	734	4746	4524	.0101	.0266	.103	.155	.0101	.0266	.103	.155	0.95	2.63
7cb	400	55	146	438	797	3851	3588	.0143	.0379	.114	.207	.0143	.0379	.114	.207	0.93	2.65
8cb	400	163	410	1037	1801	4071	3472	.0402	.1007	.255	.443	.0402	.1007	.255	.443	0.85	2.52

+ Note that no correction was made for the different sensitivity of the compounds.

→→ Photolysed for 15 mins. with no chlorine present.

Table III.26. Chlorination of Trans Dibromoethylene

Temp. = 79.5°C

Pressure of Trans Dibromoethylene ~ 5 mm Hg

Pressure of Chlorine < 1 mm Hg

Pressure of Carbon Dioxide = variable

Run No.	P _{CO2} mm Hg	Area Ratios ⁺												
		Area t DCE	Area c DCE	Area t CBE	Area c CBE	Area t DBE	Area c DBE	t DCE / t DBE	c DCE / t DBE	t CBE / t DBE	c CBE / t DBE	t DBE / t DBE	c DBE / t DBE	
1 ^{tb}	nil	-	-	-	-	3673	1766	-	-	-	-	0.48	-	-
2 ^{tb}	nil	-	-	-	-	4418	2408	-	-	-	-	0.55	-	-
3 ^{tb}	nil	nil	nil	103	181	5180	5585	-	-	.0199	.0350	1.08	-	1.70
4 ^{tb}	nil	nil	nil	141	257	5310	5910	-	-	.0266	.0485	1.11	-	1.82
5 ^{tb}	nil	nil	nil	159	272	3930	4750	-	-	.0404	.0692	1.21	-	1.71
6 ^{tb}	nil	792	2010	1349	2303	1522	1873	.52	1.32	.89	1.51	1.23	2.54	1.71
7 ^{tb}	218	+++	+++	468	830	4566	5403	+++	+++	.103	.182	1.19	+++	1.77
8 ^{tb}	218	+++	+++	189	327	5446	6496	+++	+++	.0347	.060	1.19	+++	1.73
9 ^{tb}	400	55	122	493	759	4208	3872	.131	.0290	.117	.180	0.92	2.22	1.54
10 ^{tb}	400	45	111	563	916	4268	4013	.0105	.0260	.132	.215	0.94	2.40	1.63
11 ^{tb}	400	106	337	916	1162	2917	3187	.0363	.115	.314	.398	1.09	3.18	1.27

+ Note that no correction was made for the different sensitivity of the compounds.

++ Photolysed for 15 mins. with no chlorine present.

+++ 3 mm chlorine used: 95 units of tetrachloroethane also formed.

++++ Peaks obscured by tail of the CO₂ peak: in subsequent runs CO₂ distilled off at -120°C.

FIG.III.2

DEPENDENCE OF R_{nPrCl}^{TCE} AND R_{nPrCl}^{tDCE} ON
 PROPANE / CIS DICHLOROETHYLENE RATIO

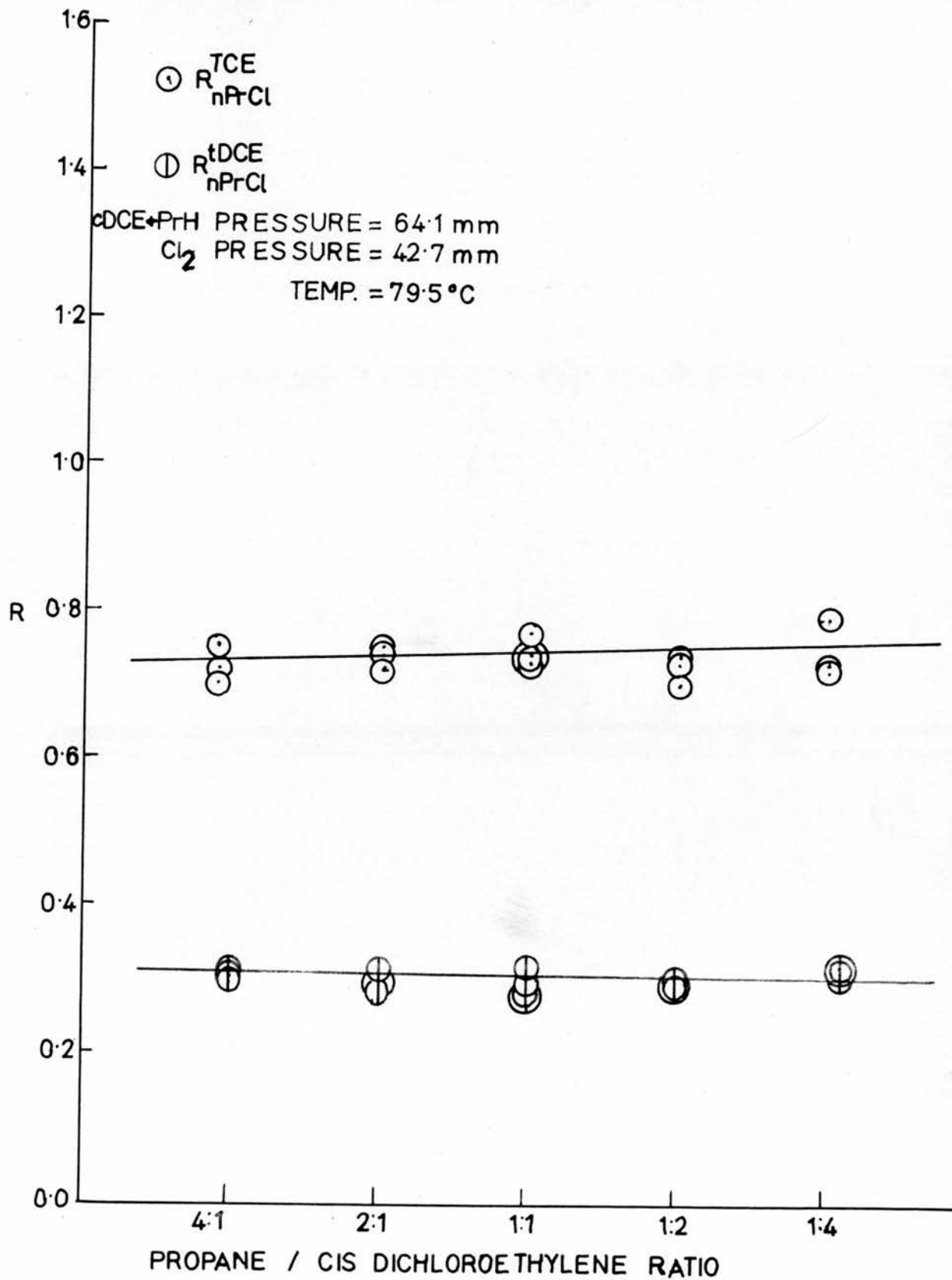


FIG.III.3

DEPENDENCE OF R_{nPrCl}^{TCE} AND R_{nPrCl}^{tDCE} ON
MIX. PRESSURE

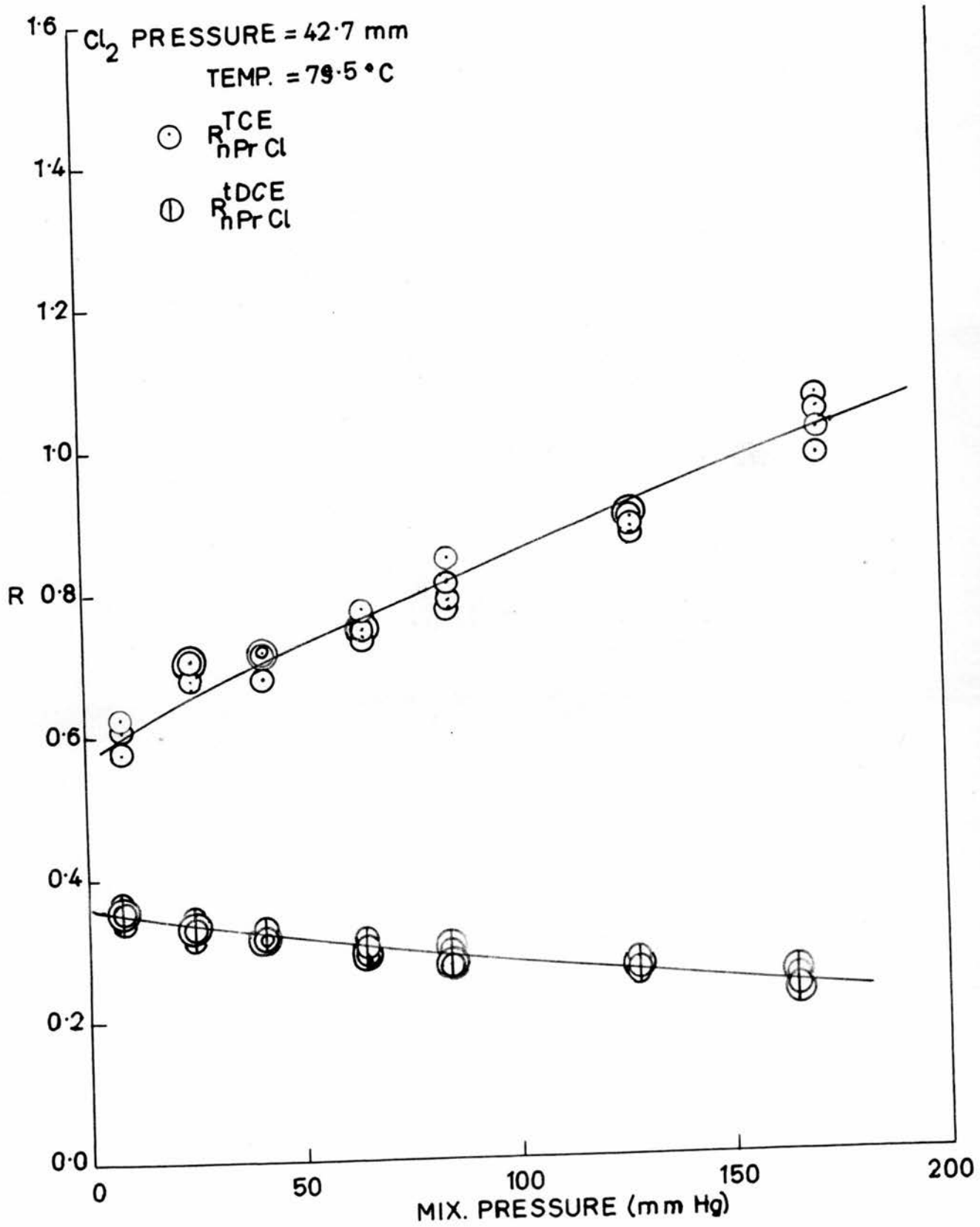


FIG. III. 4

DEPENDENCE OF R_{nPrCl}^{TCE} AND R_{nPrCl}^{tDCE} ON
 CIS DICHLOROETHYLENE PRESSURE

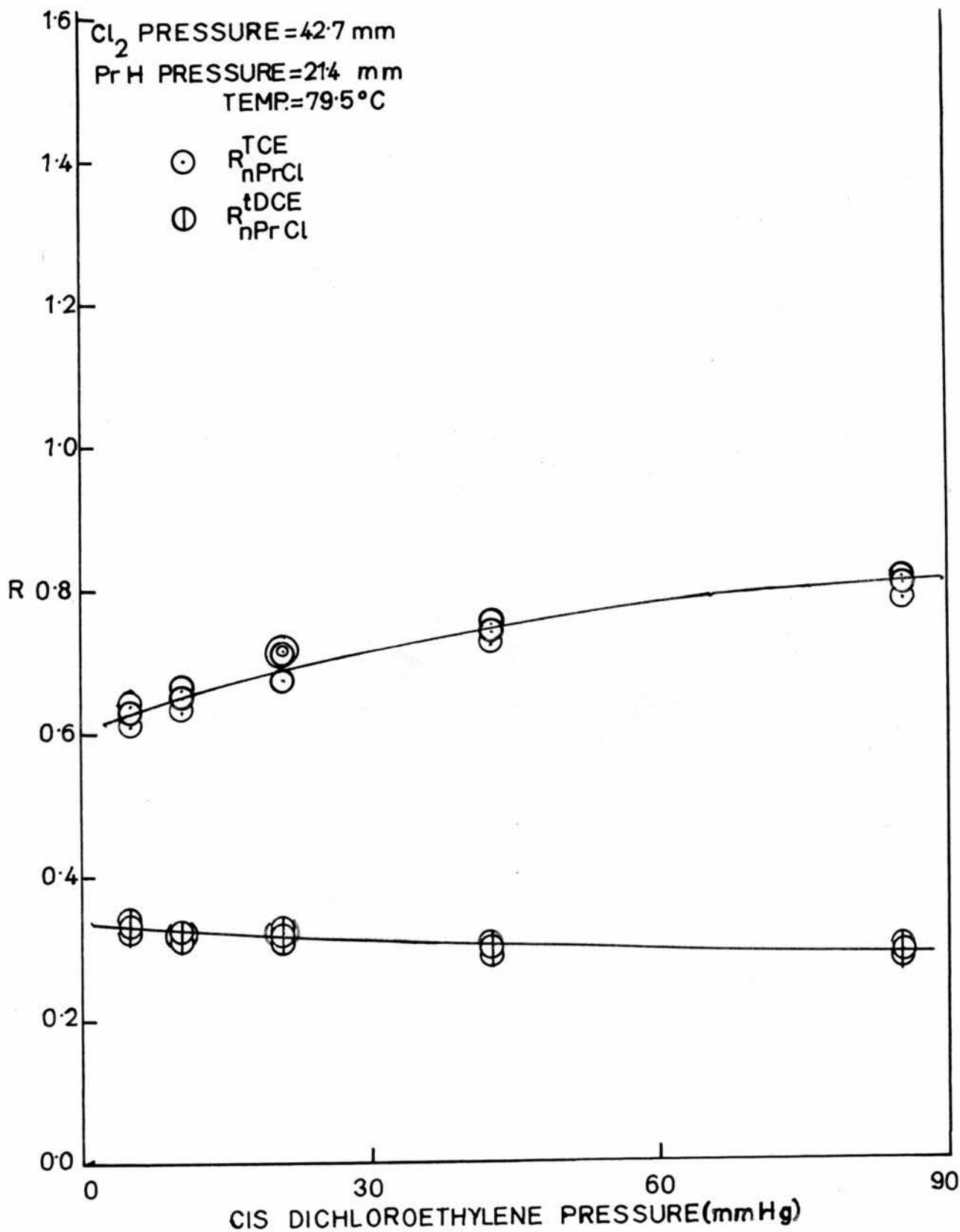


FIG.III.5

DEPENDENCE OF R_{nPrCl}^{TCE} AND R_{nPrCl}^{tDCE} ON
PROPANE PRESSURE

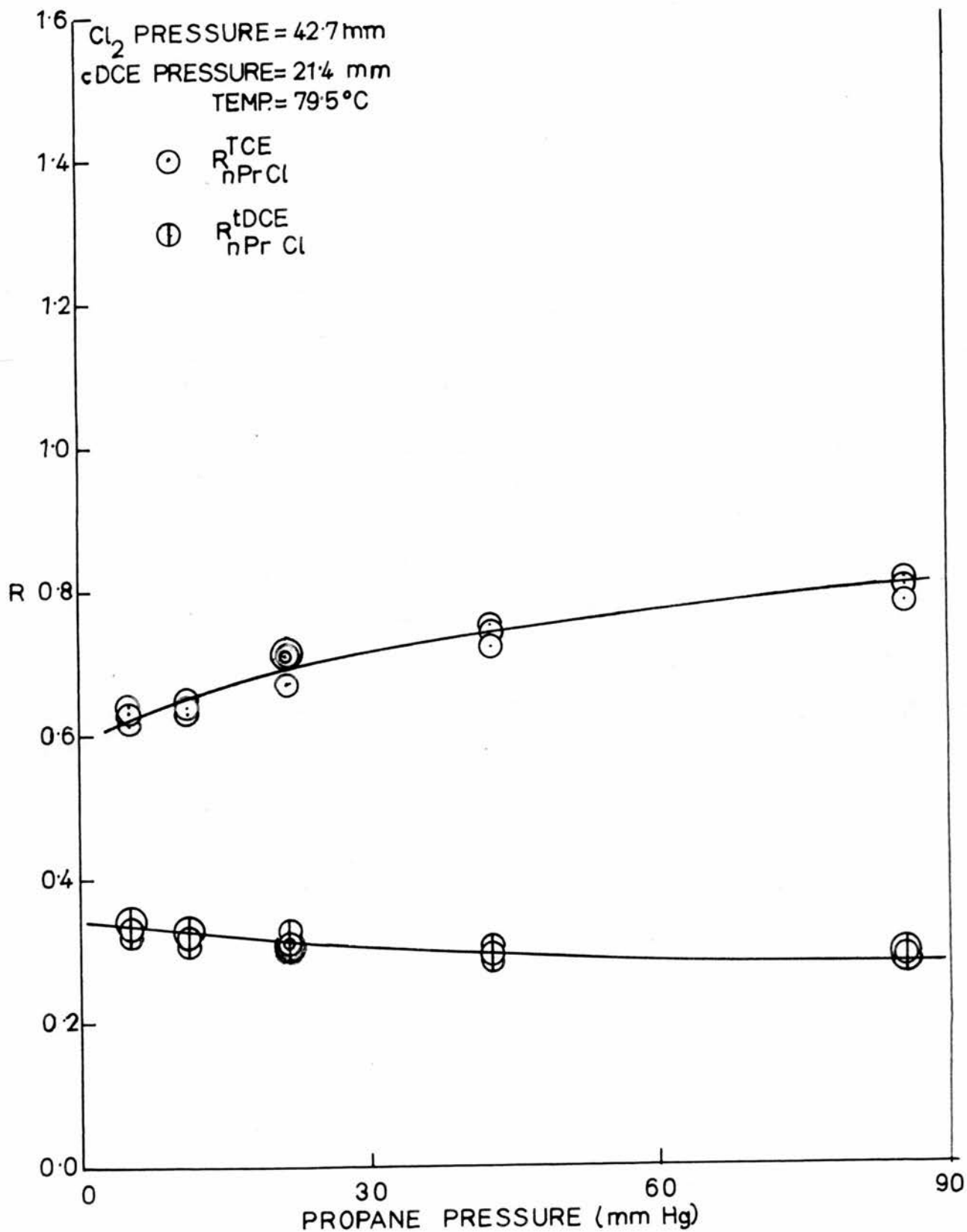


FIG. III. 6

DEPENDENCE OF R_{nPrCl}^{TCE} AND R_{nPrCl}^{tDCE} ON
CHLORINE PRESSURE

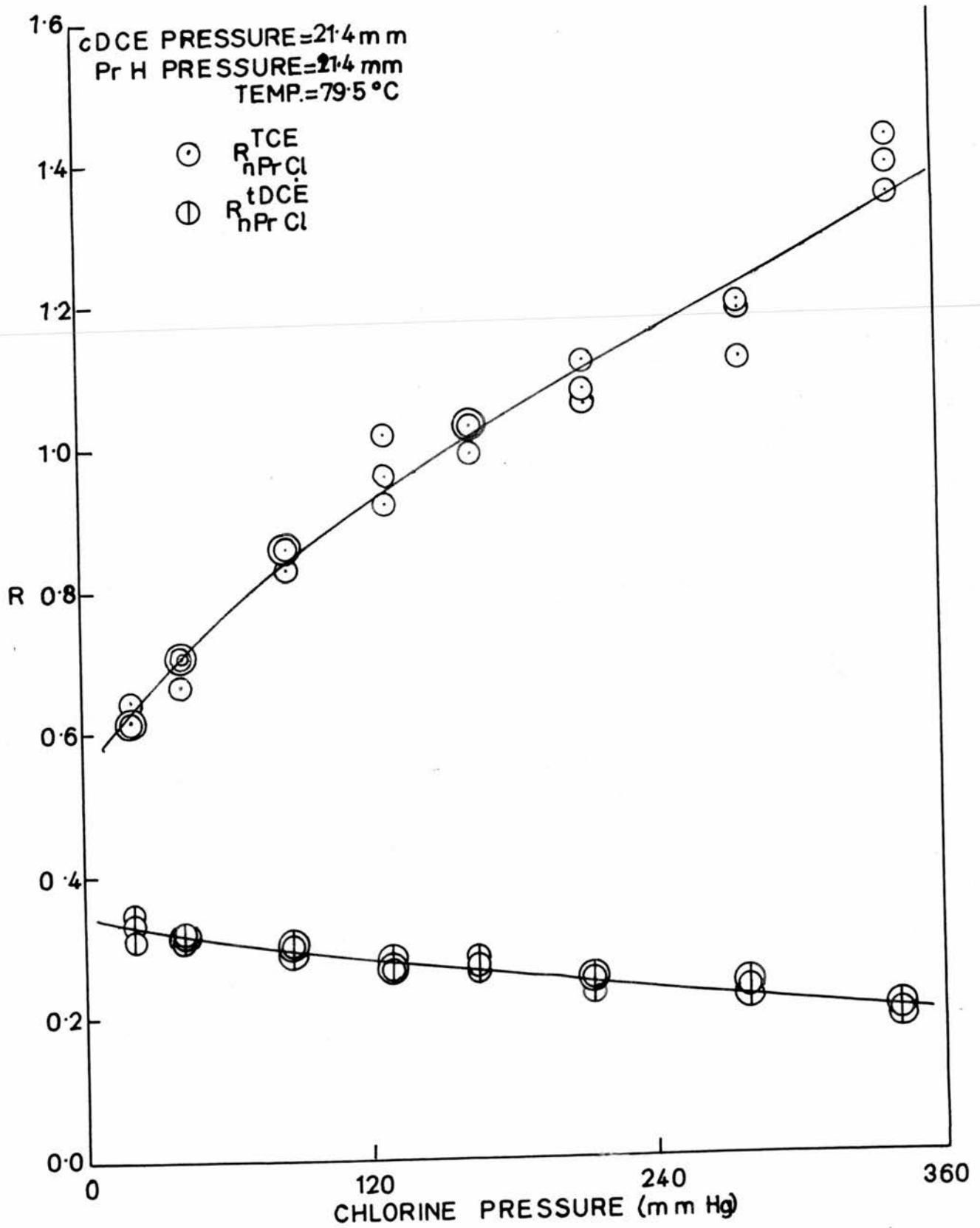
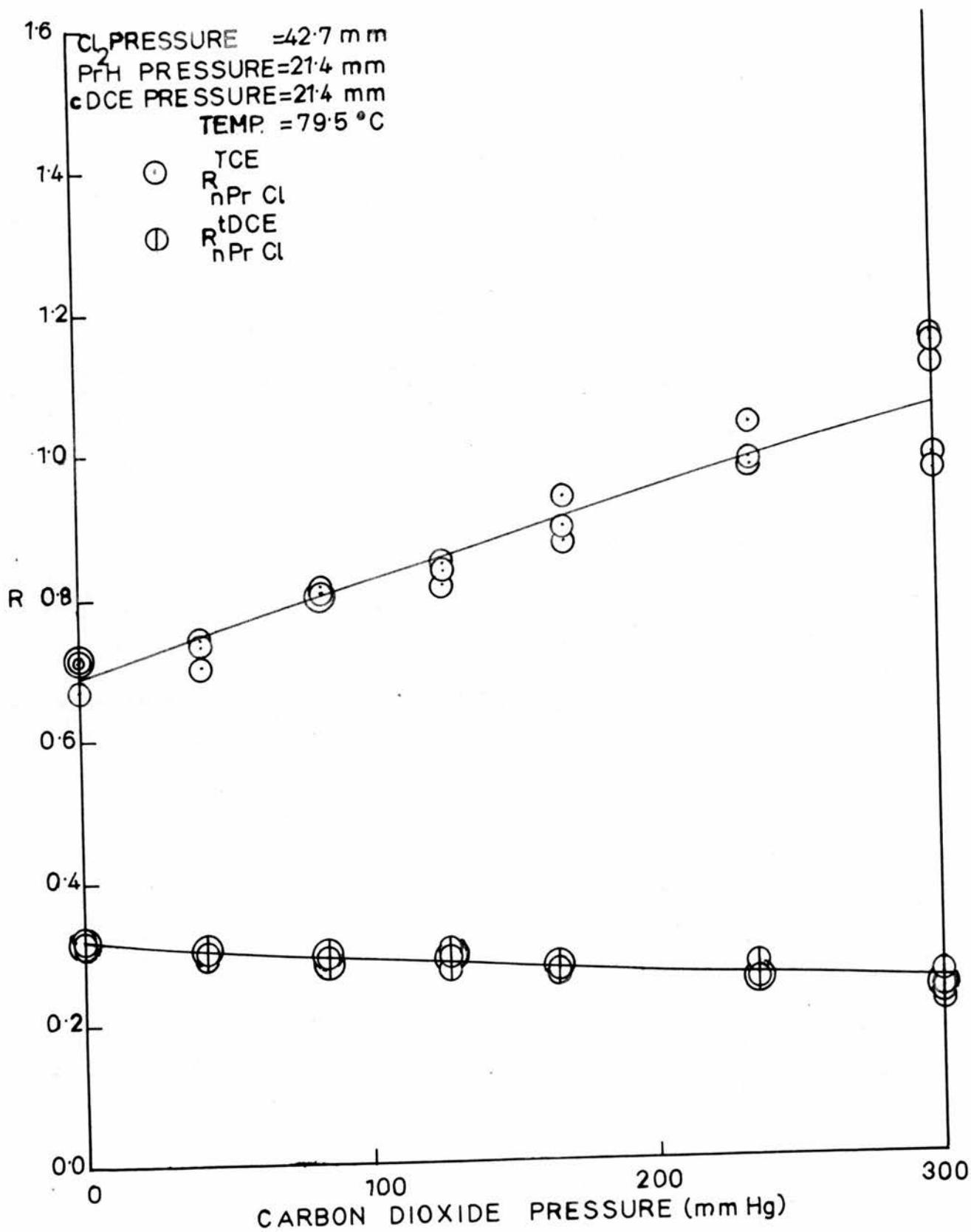


FIG. III.7

DEPENDENCE OF R_{nPrCl}^{TCE} AND R_{nPrCl}^{tDCE} ON
CARBON DIOXIDE PRESSURE



DEPENDENCE OF R_{nPrCl}^{TCE} AND R_{nPrCl}^{cDCE} ON
PROPANE / TRANS DICHLOROETHYLENE RATIO

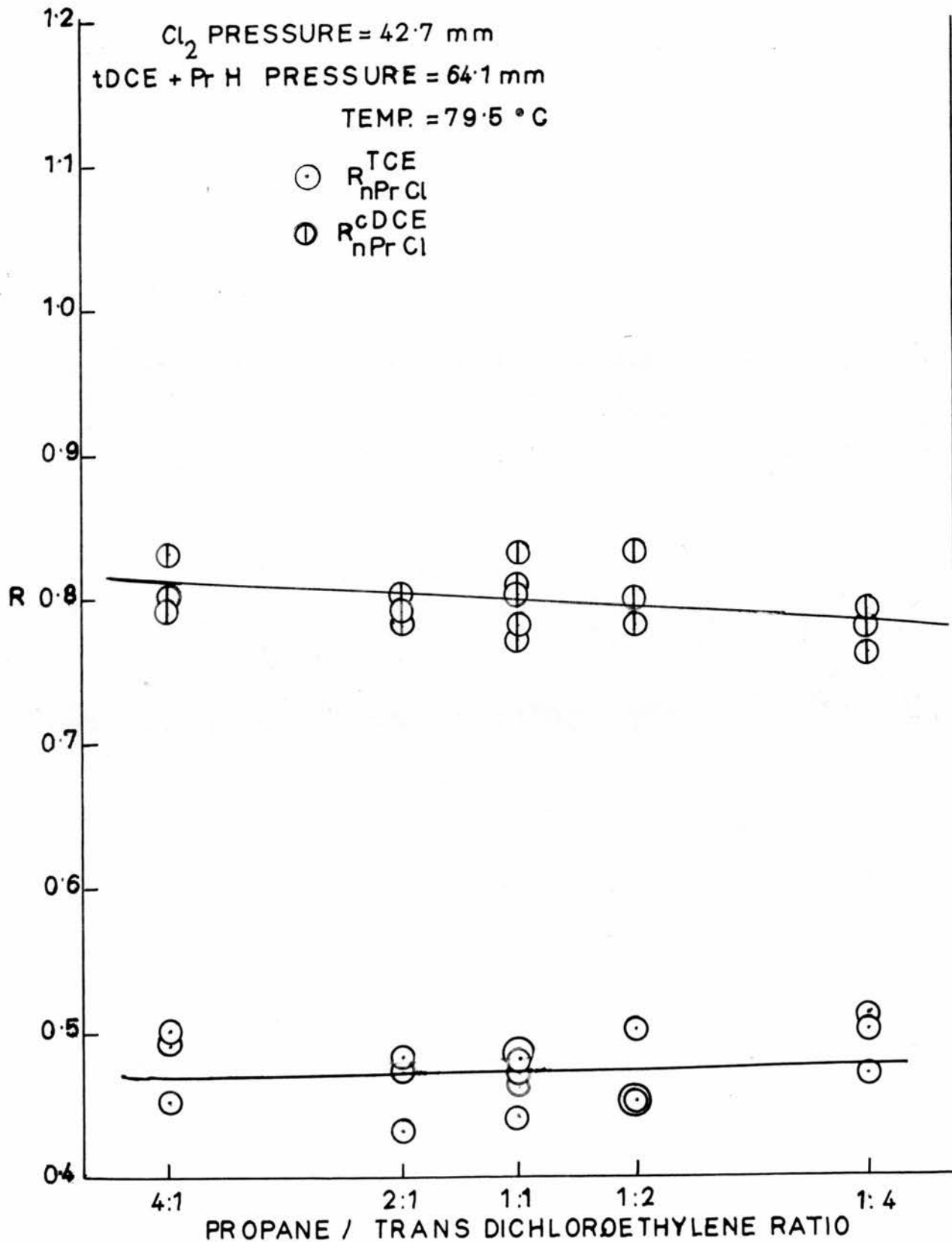


FIG. 11.11

DEPENDENCE OF R_{nPrCl}^{TCE} AND R_{nPrCl}^{cDCE} ON
MIX. PRESSURE

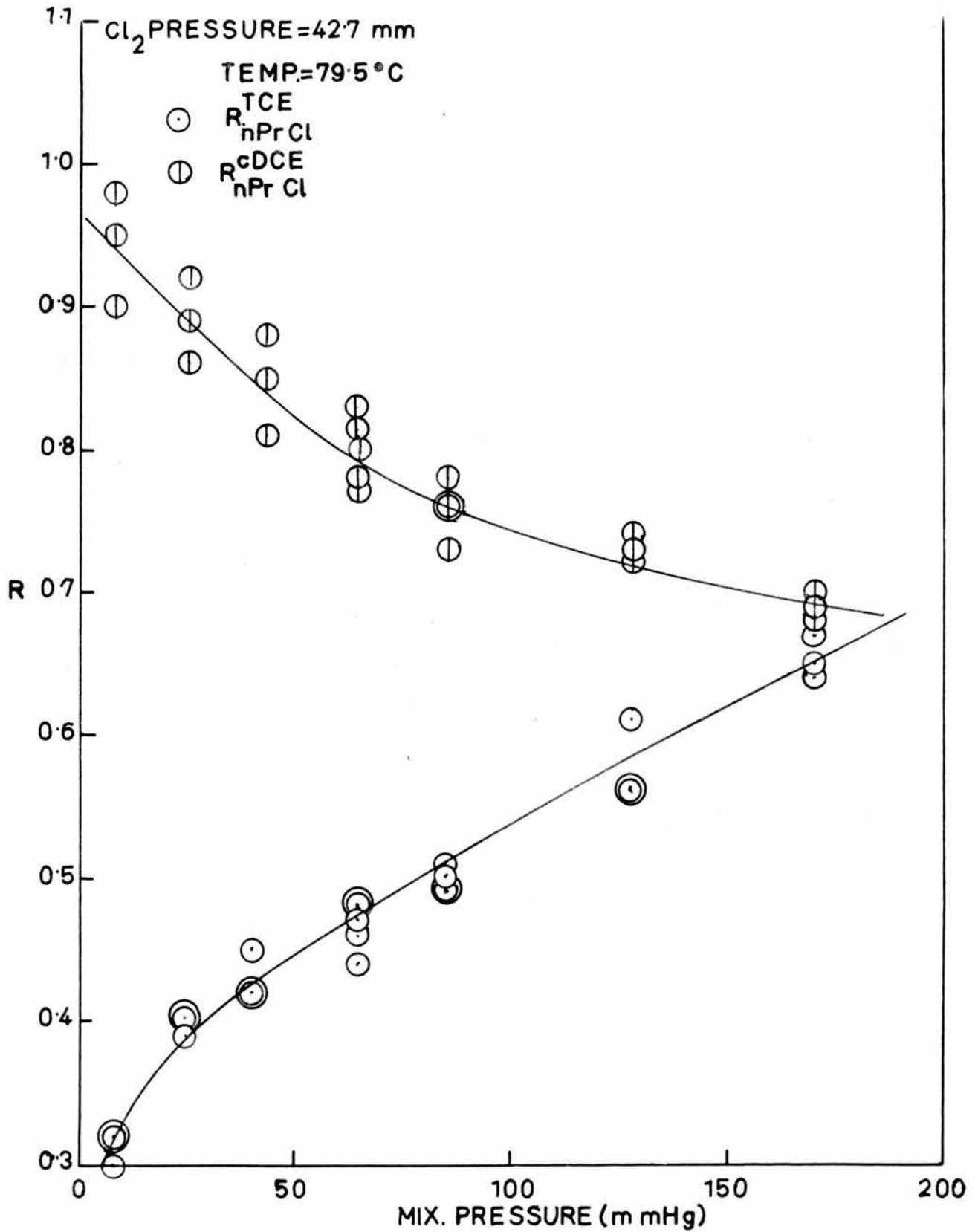


FIG. III.12

DEPENDENCE OF R_{nPrCl}^{TCE} AND R_{nPrCl}^{cDCE} ON
TRANS DICHLOROETHYLENE PRESSURE

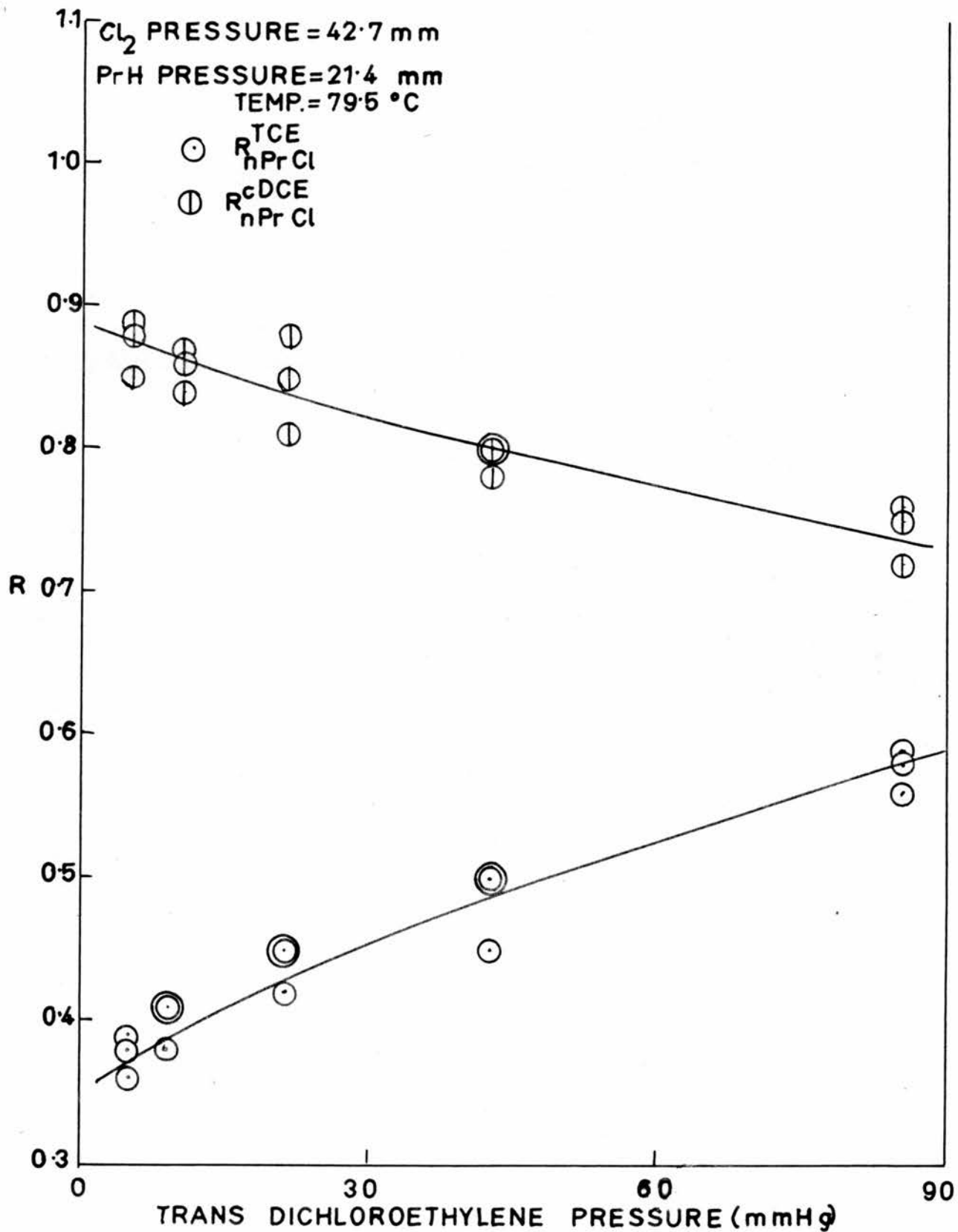


FIG III.13

DEPENDENCE OF R_{nPrCl}^{TCE} AND R_{nPrCl}^{cDCE} ON
PROPANE PRESSURE

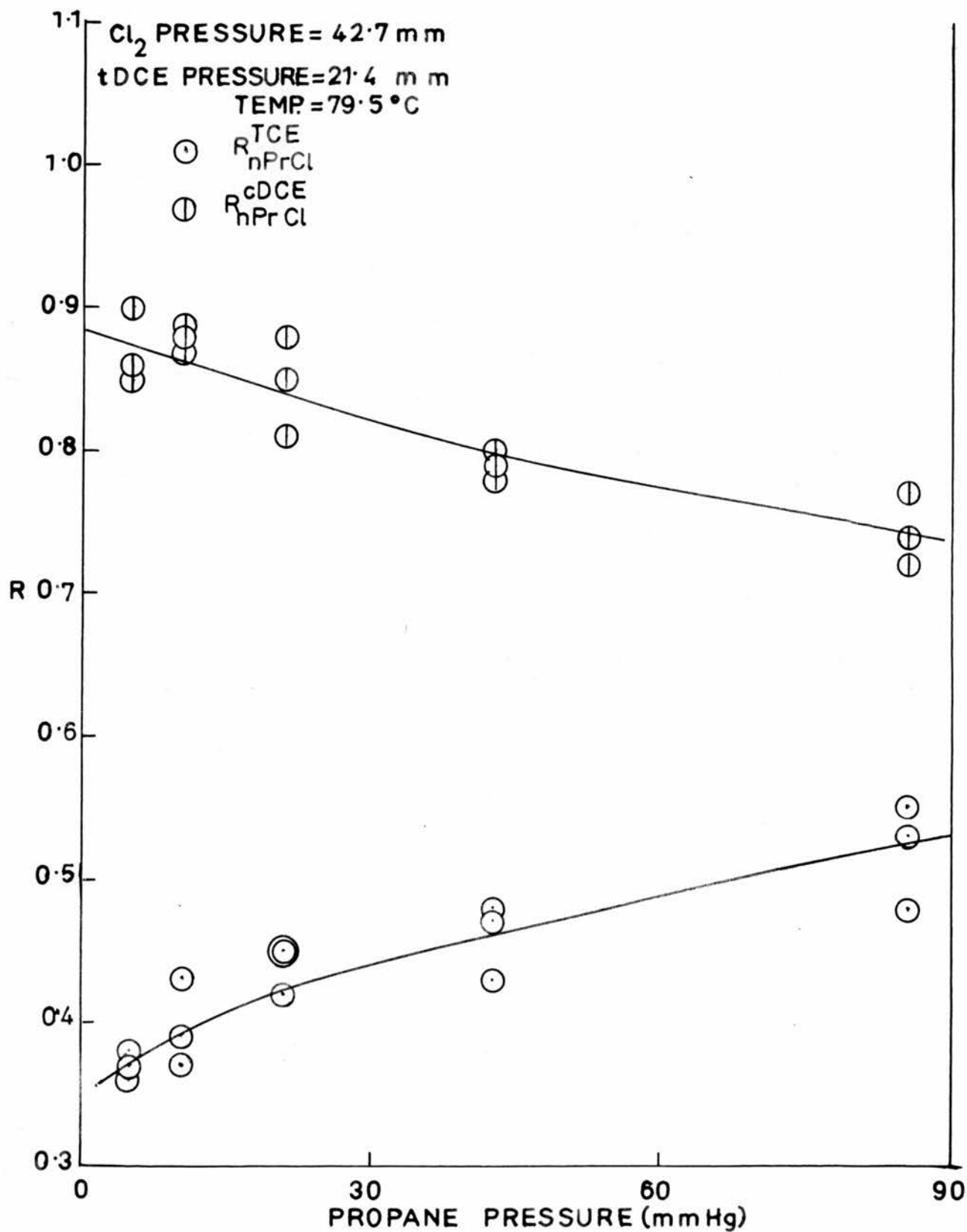
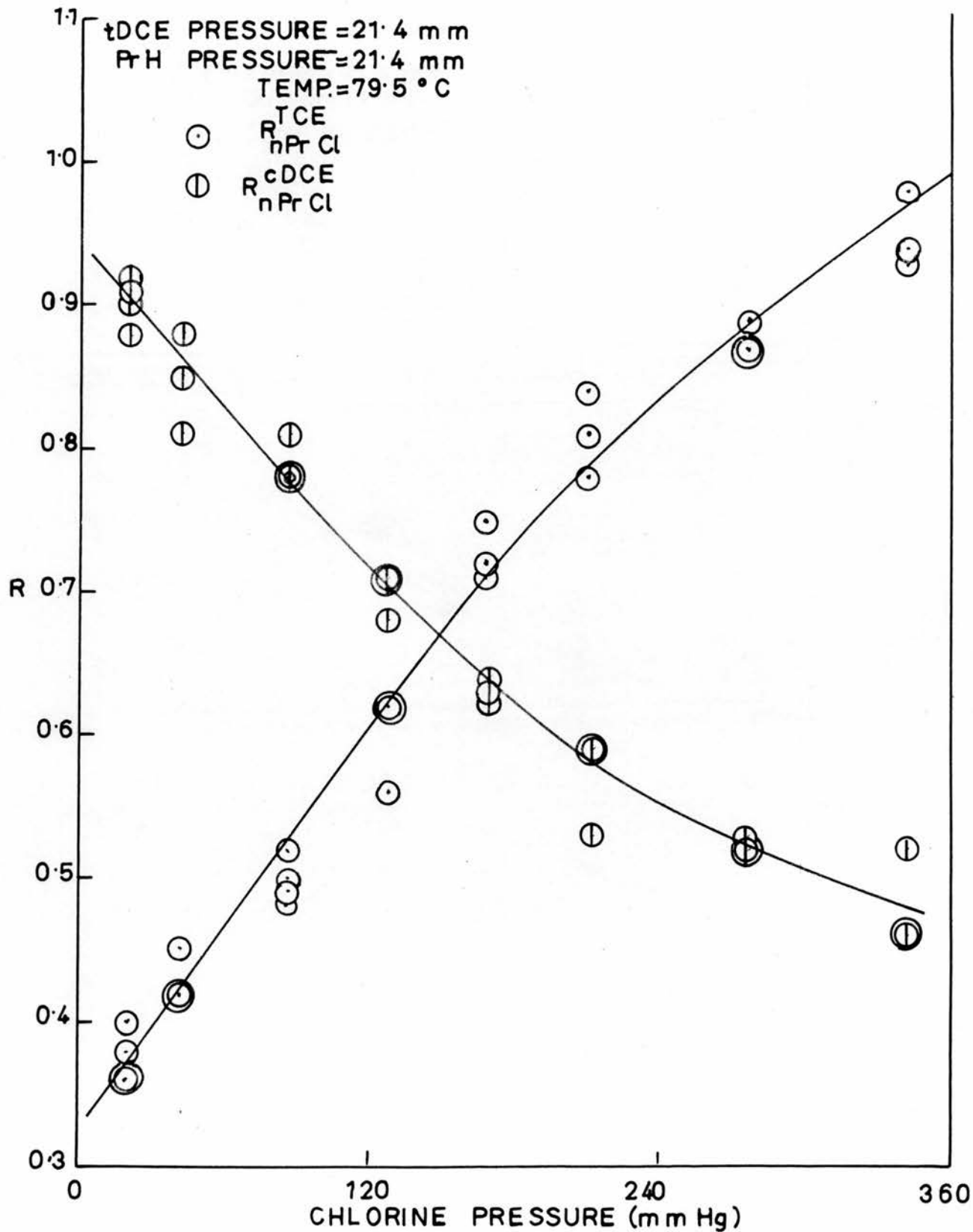
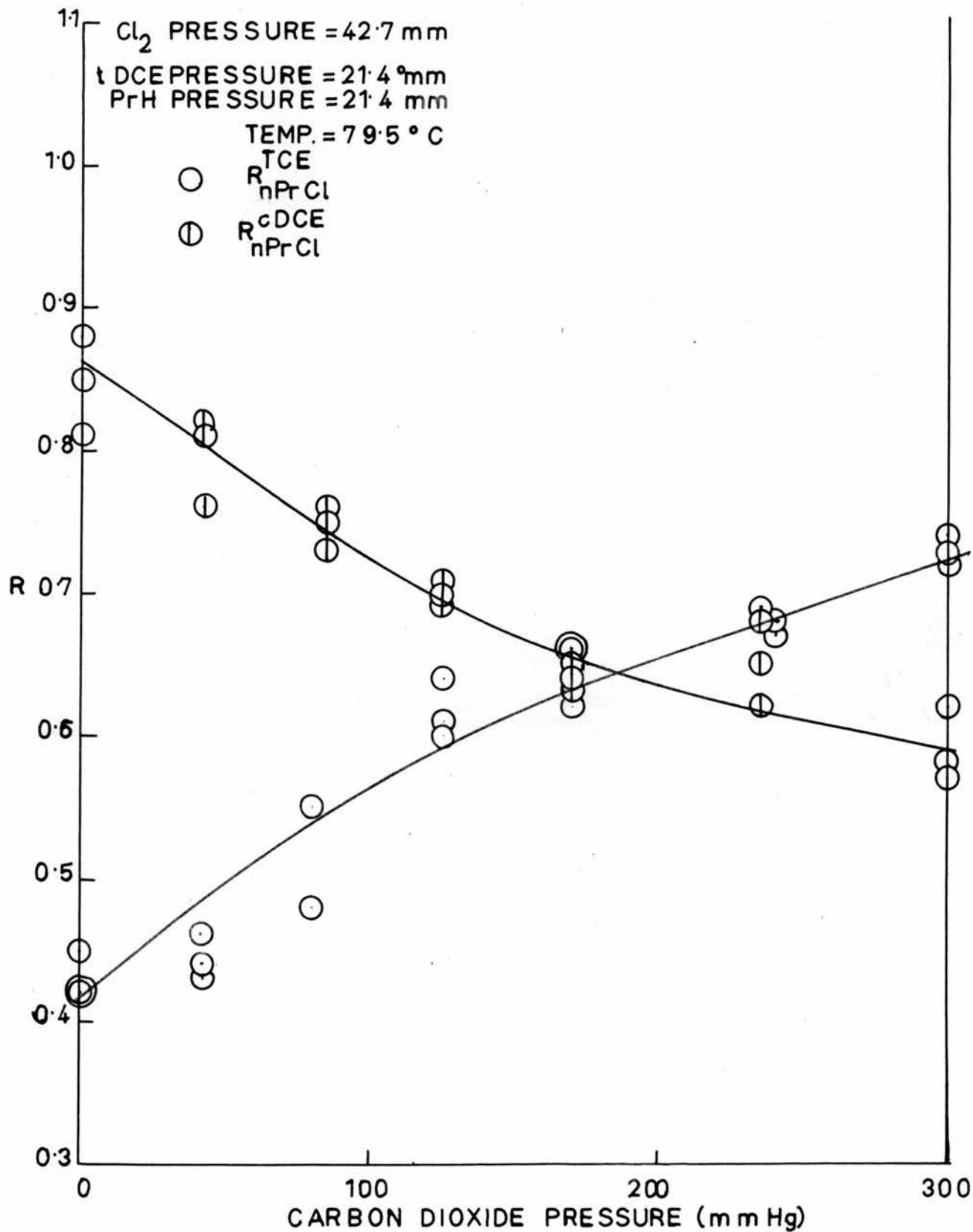


FIG. III.14

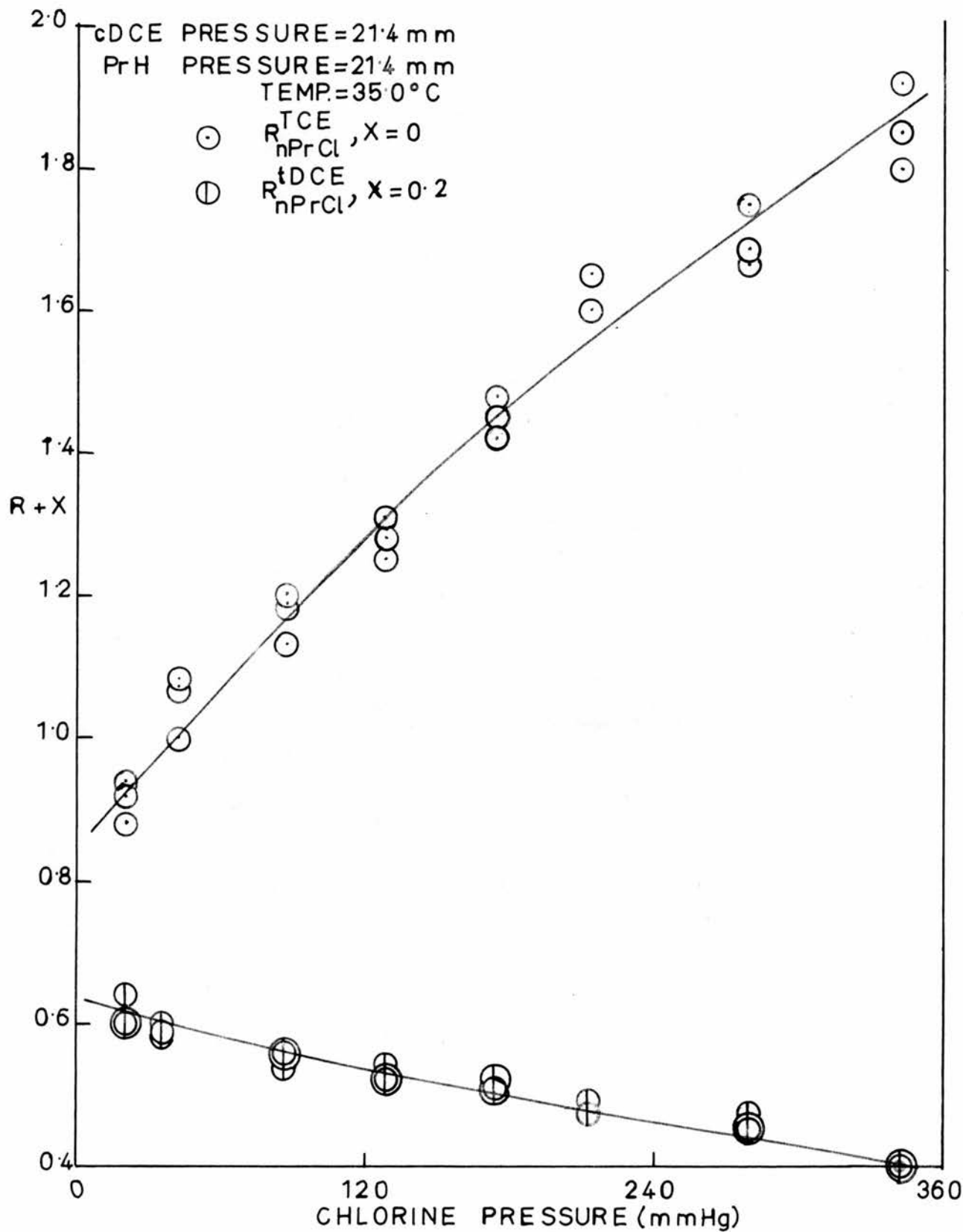
DEPENDENCE OF $R_{nPr Cl}^{TCE}$ AND $R_{nPr Cl}^{cDCE}$ ON
CHLORINE PRESSURE



DEPENDENCE OF R_{nPrCl}^{TCE} AND R_{nPrCl}^{cDCE} ON
CARBON DIOXIDE PRESSURE



DEPENDENCE OF R_{nPrCl}^{TCE} AND R_{nPrCl}^{tDCE} ON
CHLORINE PRESSURE



DEPENDENCE OF R_{nPrCl}^{TCE} AND R_{nPrCl}^{tDCE} ON
CHLORINE PRESSURE

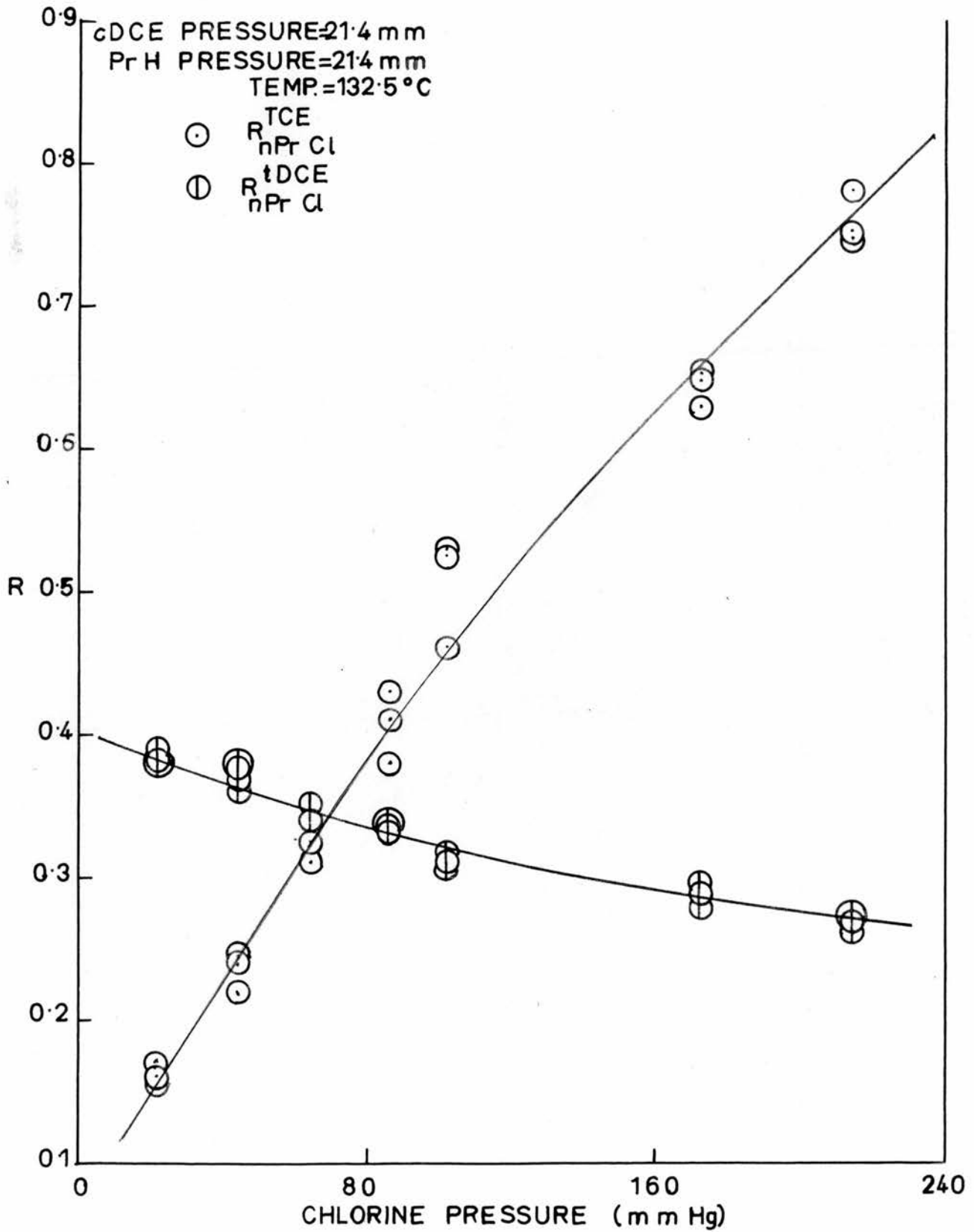


FIG. III.21

DEPENDENCE OF R_{nPrCl}^{TCE} AND R_{nPrCl}^{cDCE} ON
CHLORINE PRESSURE

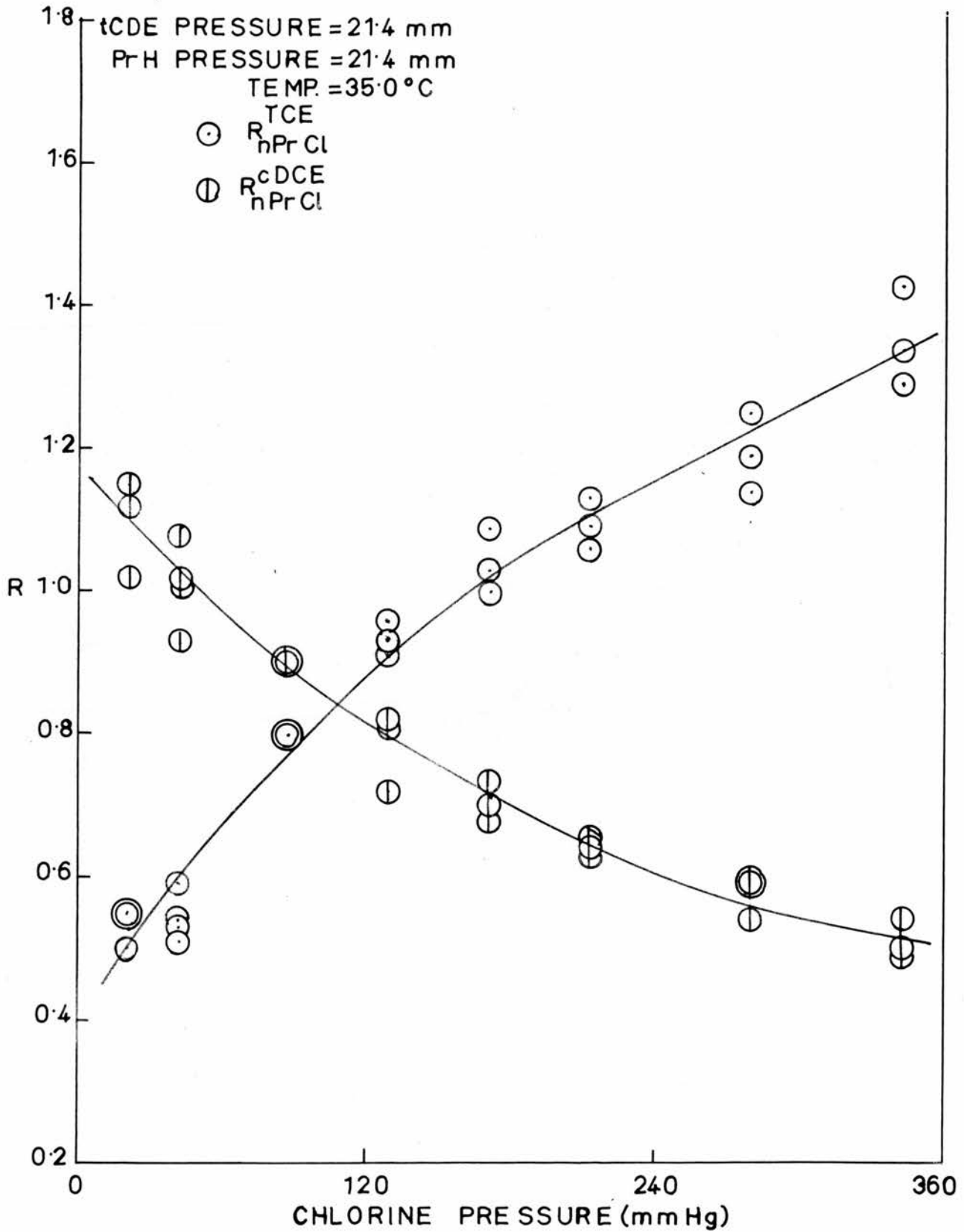


FIG. III .22

DEPENDENCE OF R_{nPrCl}^{TCE} AND R_{nPrCl}^{cDCE} ON CHLORINE PRESSURE

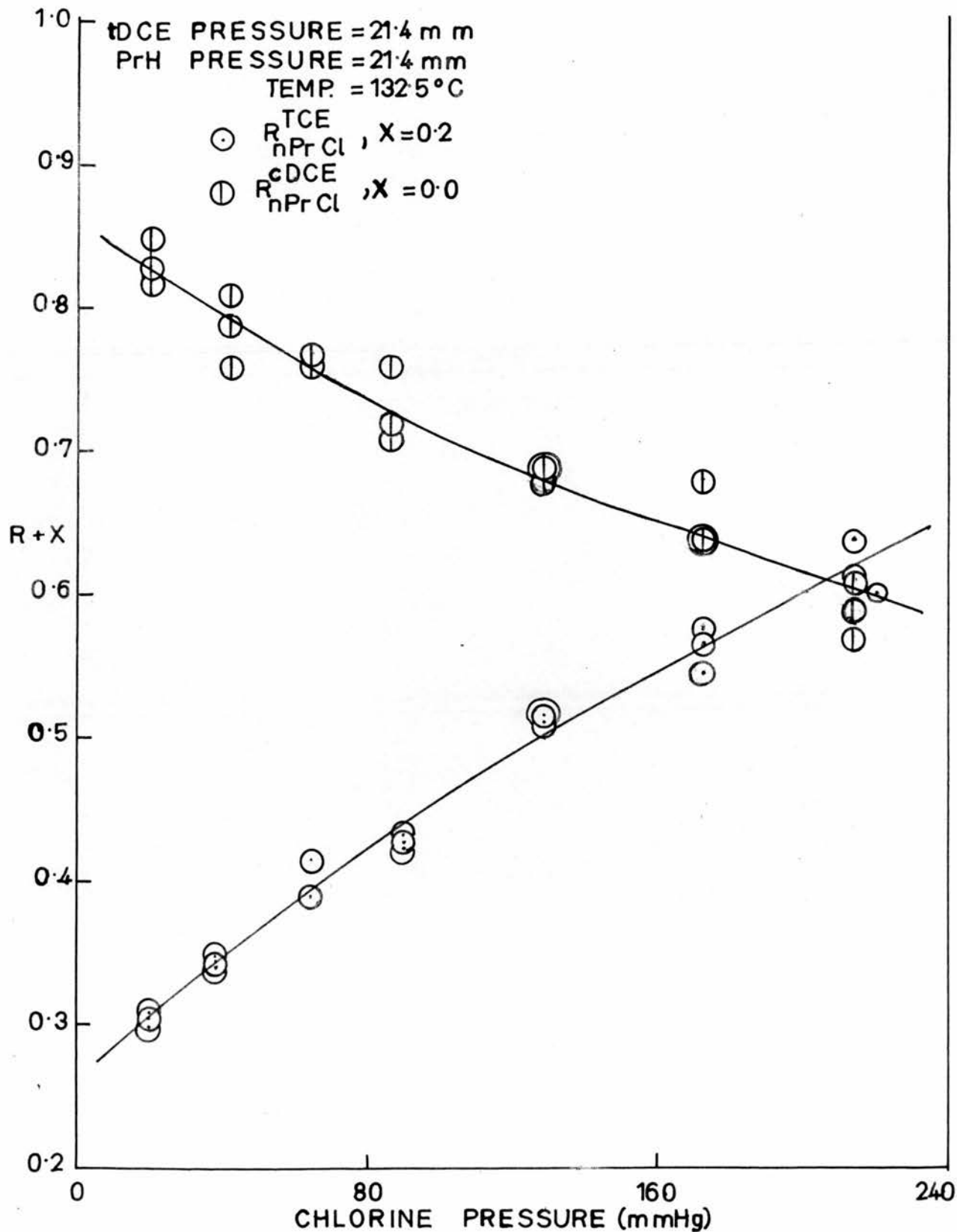
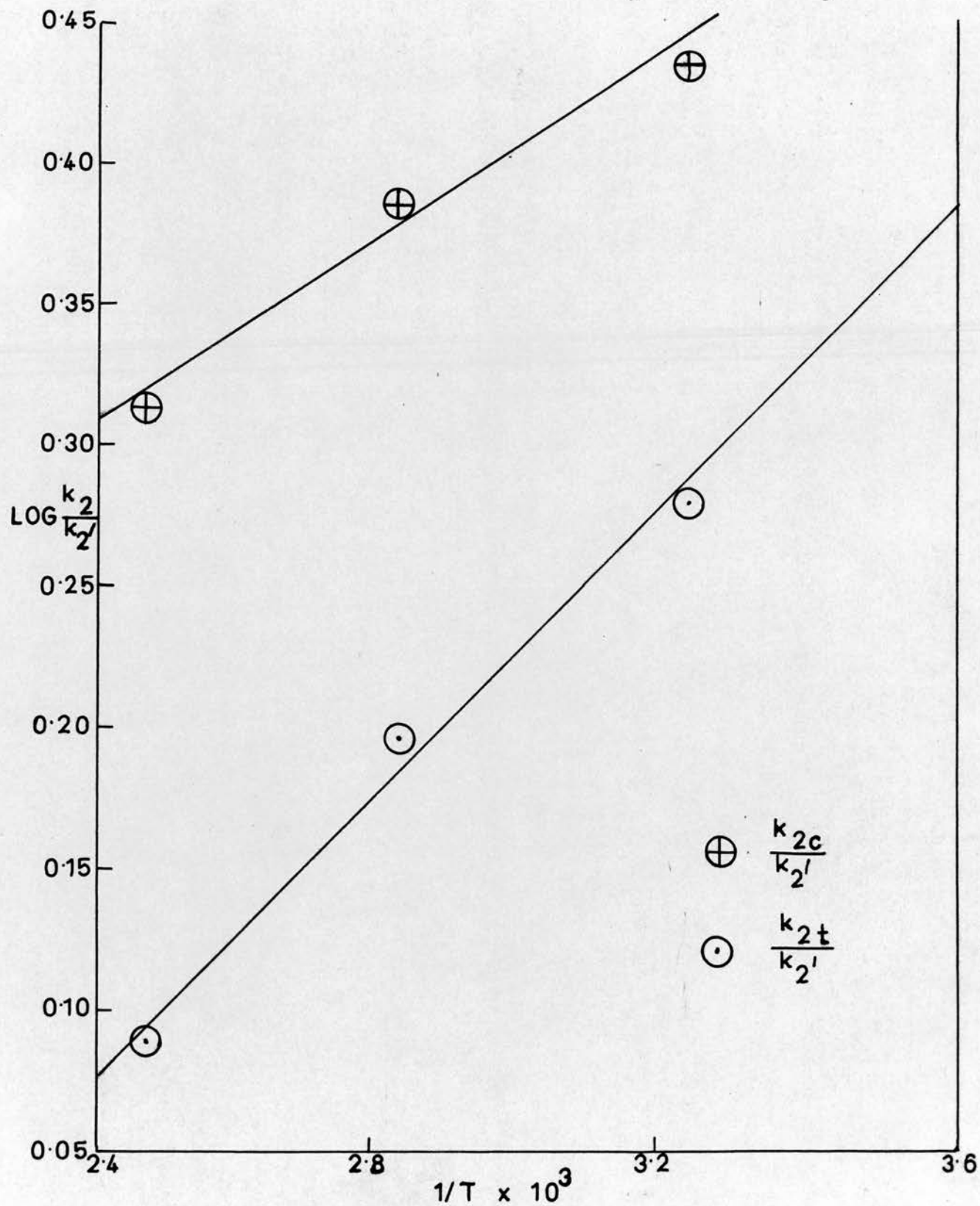


FIG. III.23

ARRHENIUS PLOTS FOR $\frac{k_{2c}}{k_{2'}}$ and $\frac{k_{2t}}{k_{2'}}$



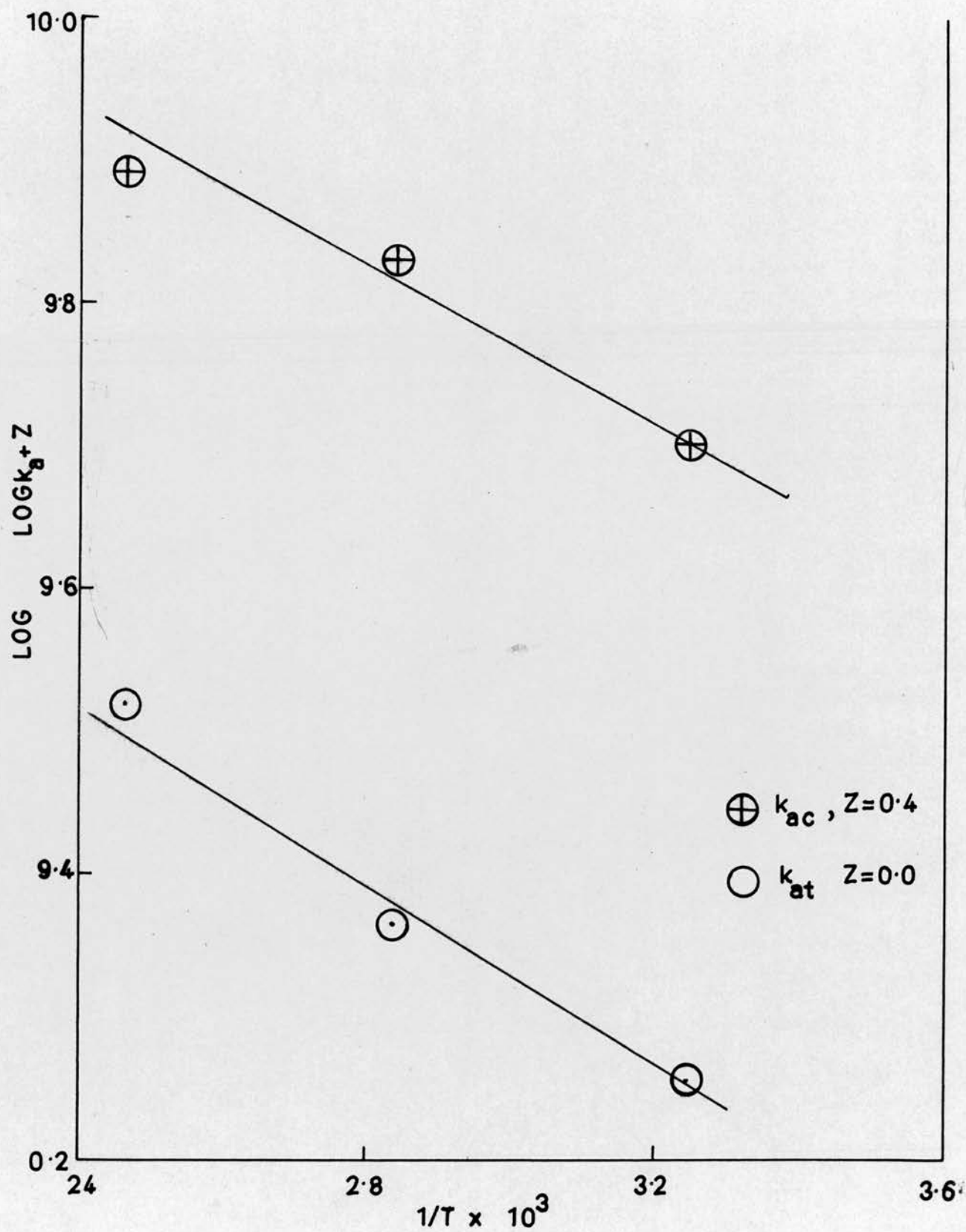
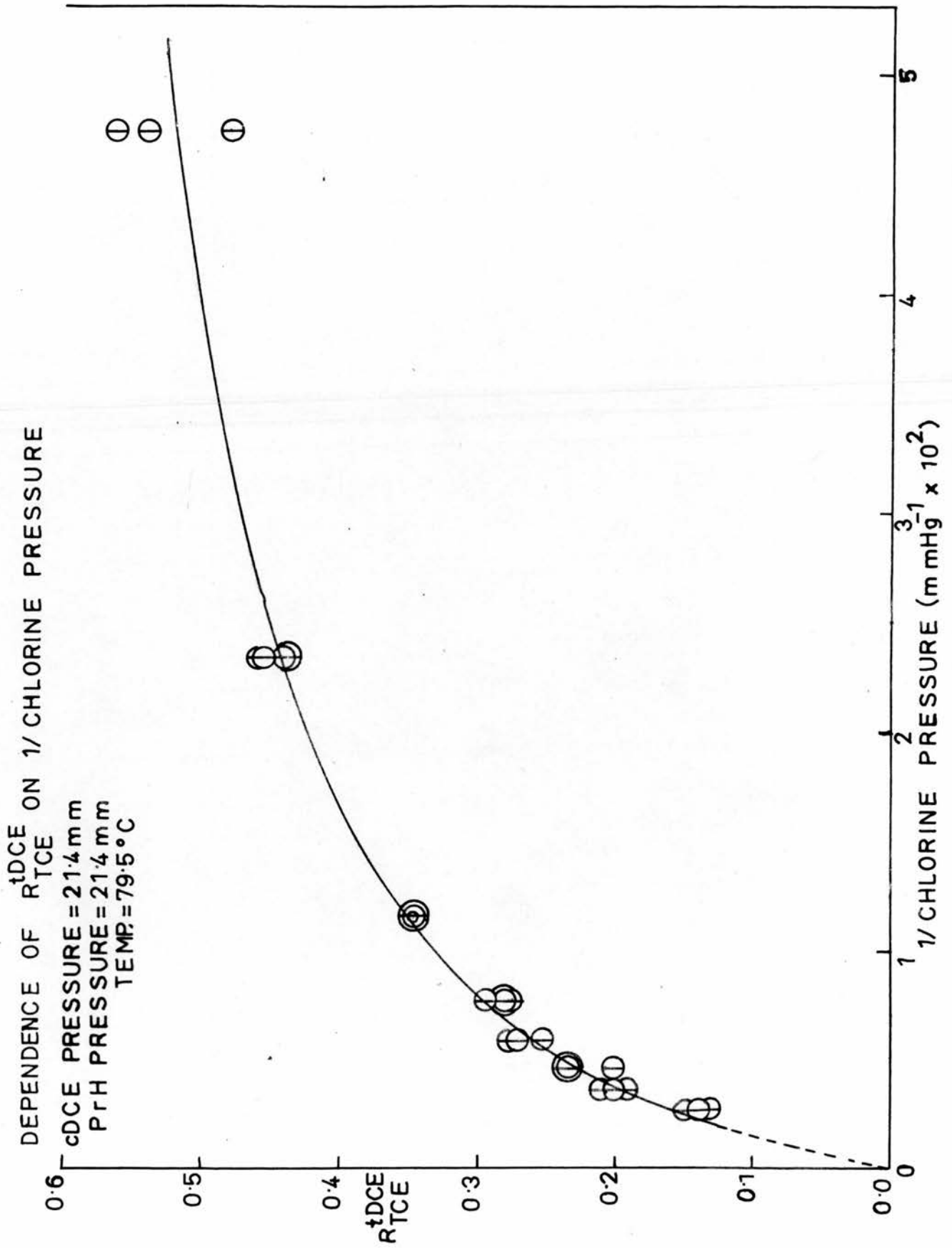
ARRHENIUS PLOTS FOR k_{ac} and k_{at} 

FIG. III.6a



DEPENDENCE OF R_{TCE}^{tDCE} ON 1/REACTANT PRESSURE AT 79.5°C

FIG. III.8 a

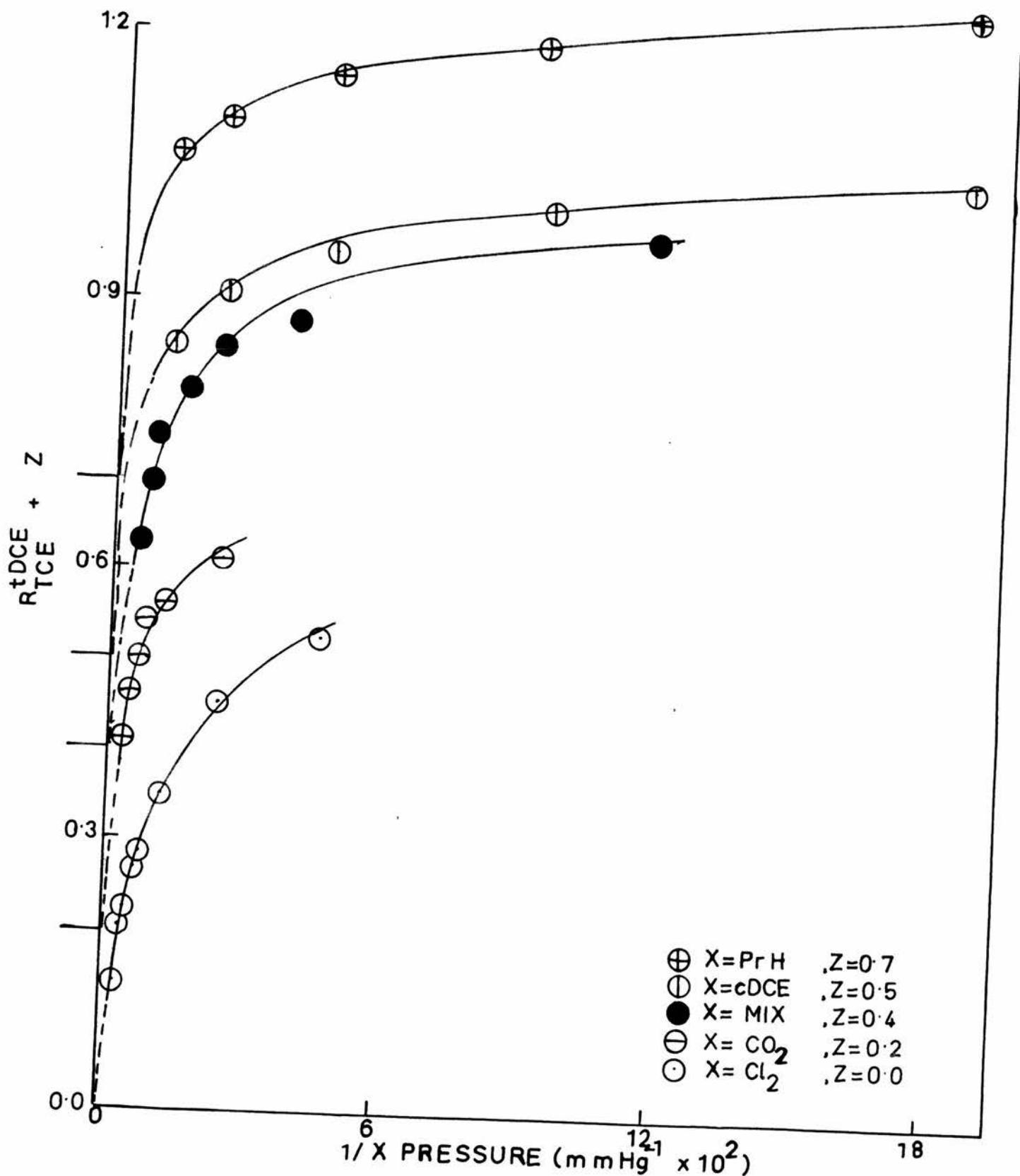


FIG. III 14a

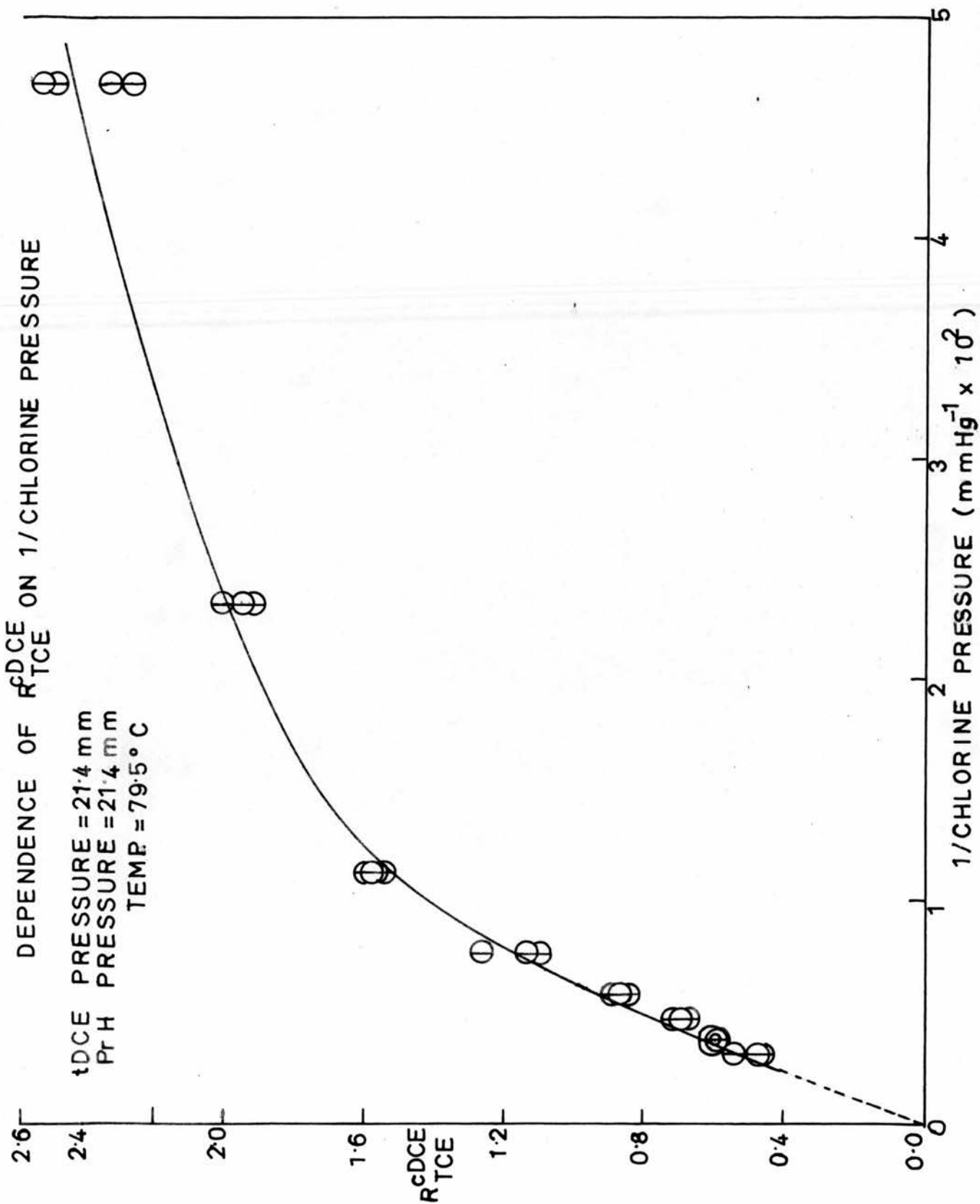


FIG. III.16 a

DEPENDENCE OF R_{TCE}^{cDCE} ON 1/REACTANT PRESSURE AT 79.5°C

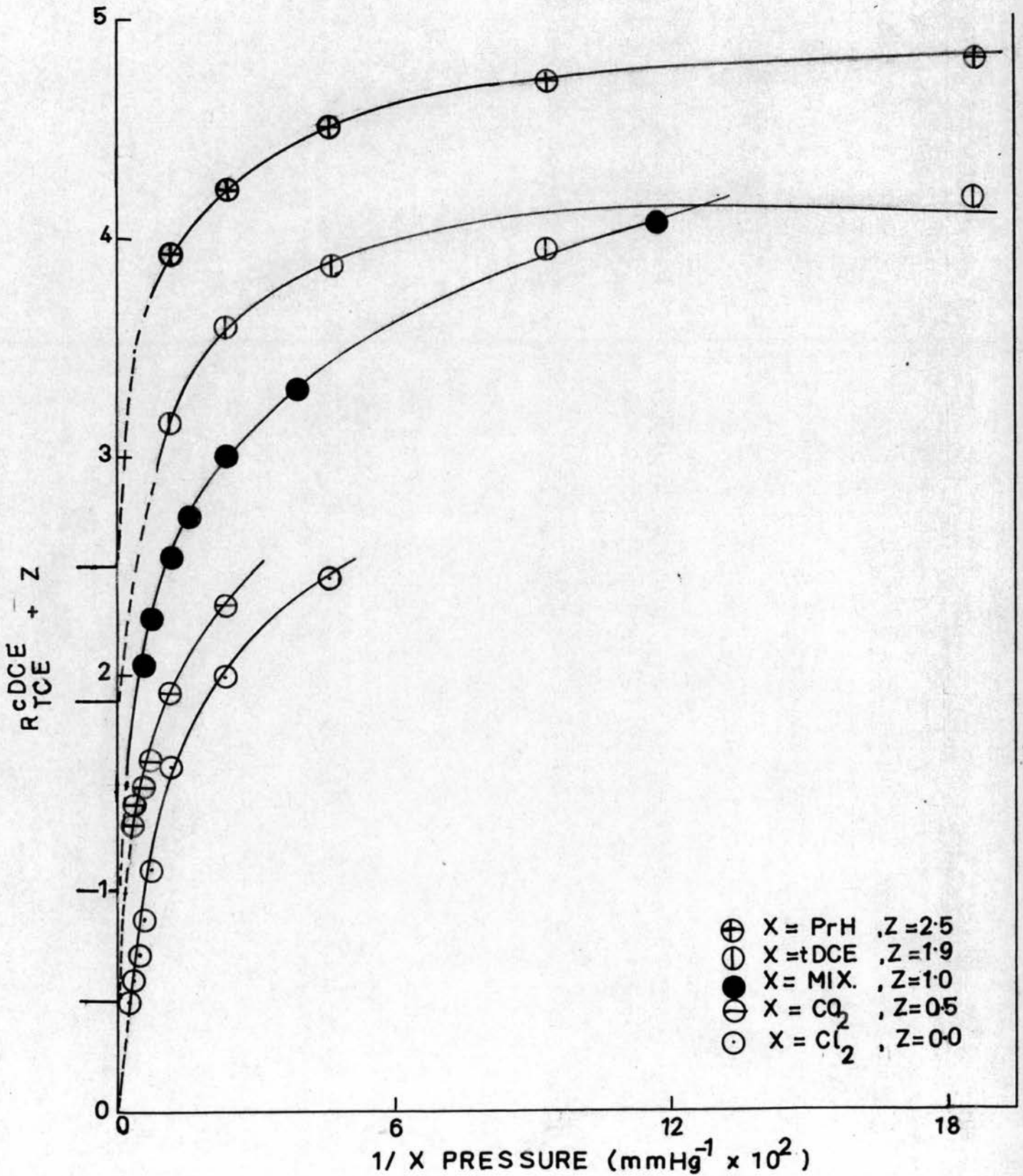


FIG. III.19a

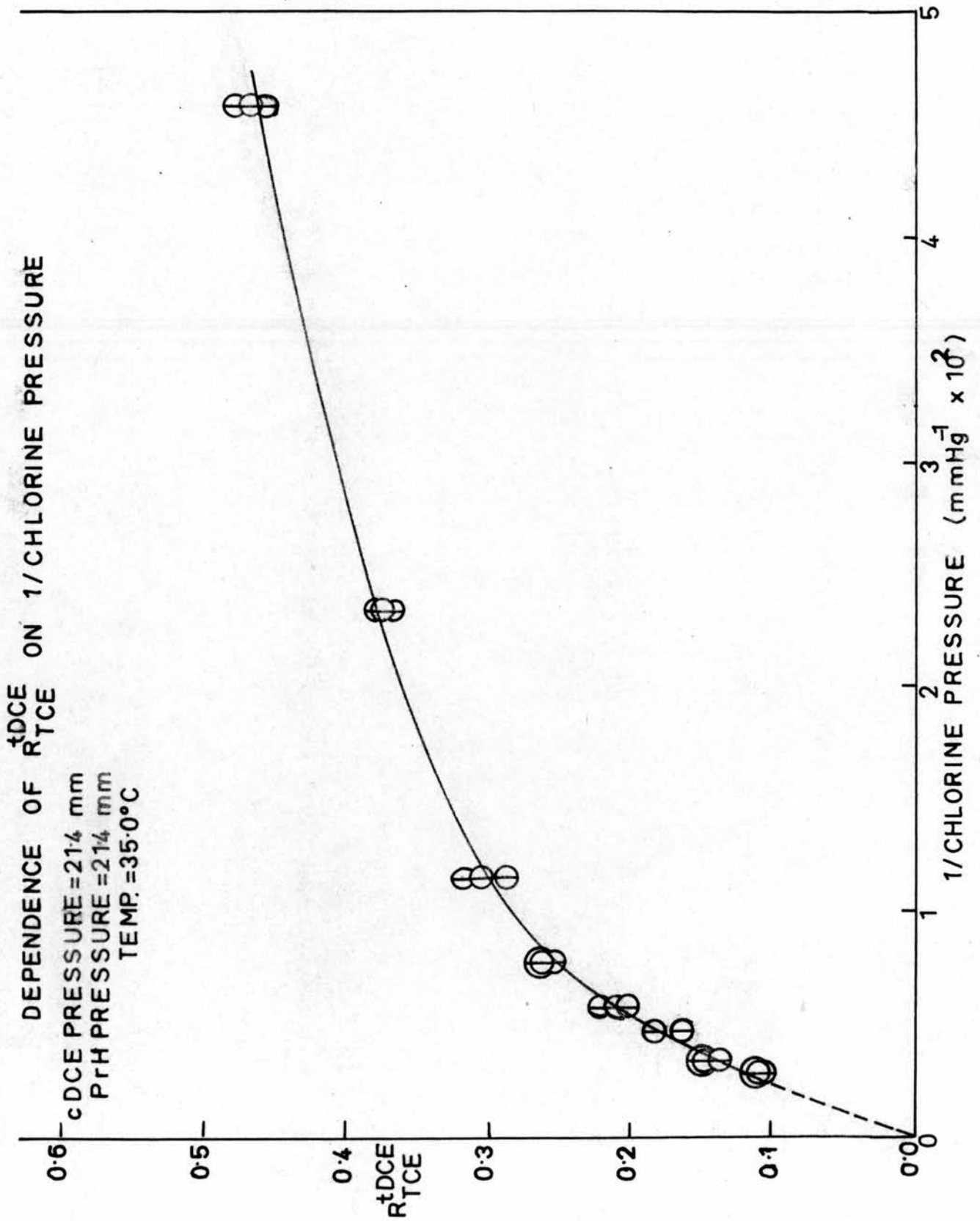
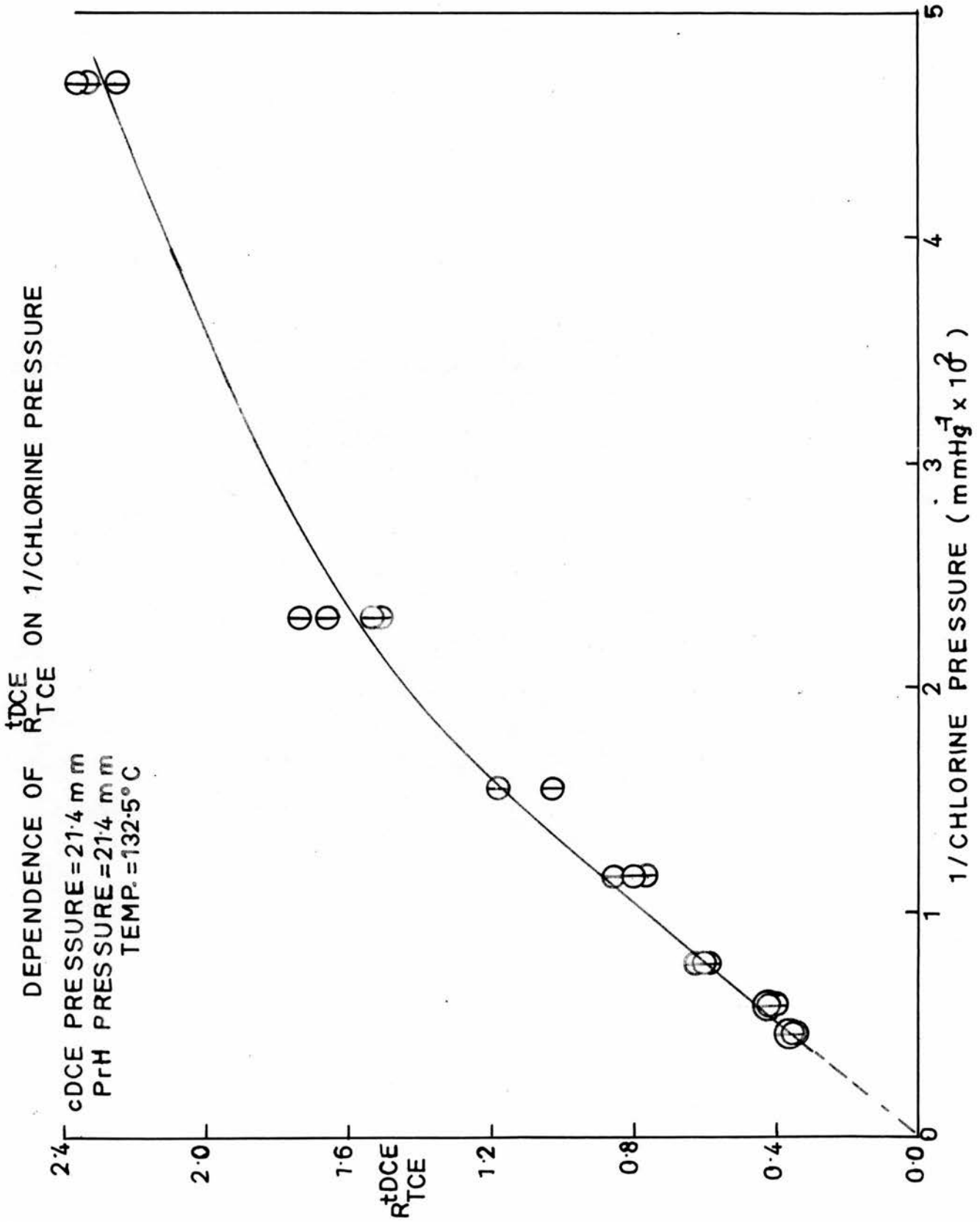


FIG. III.20a



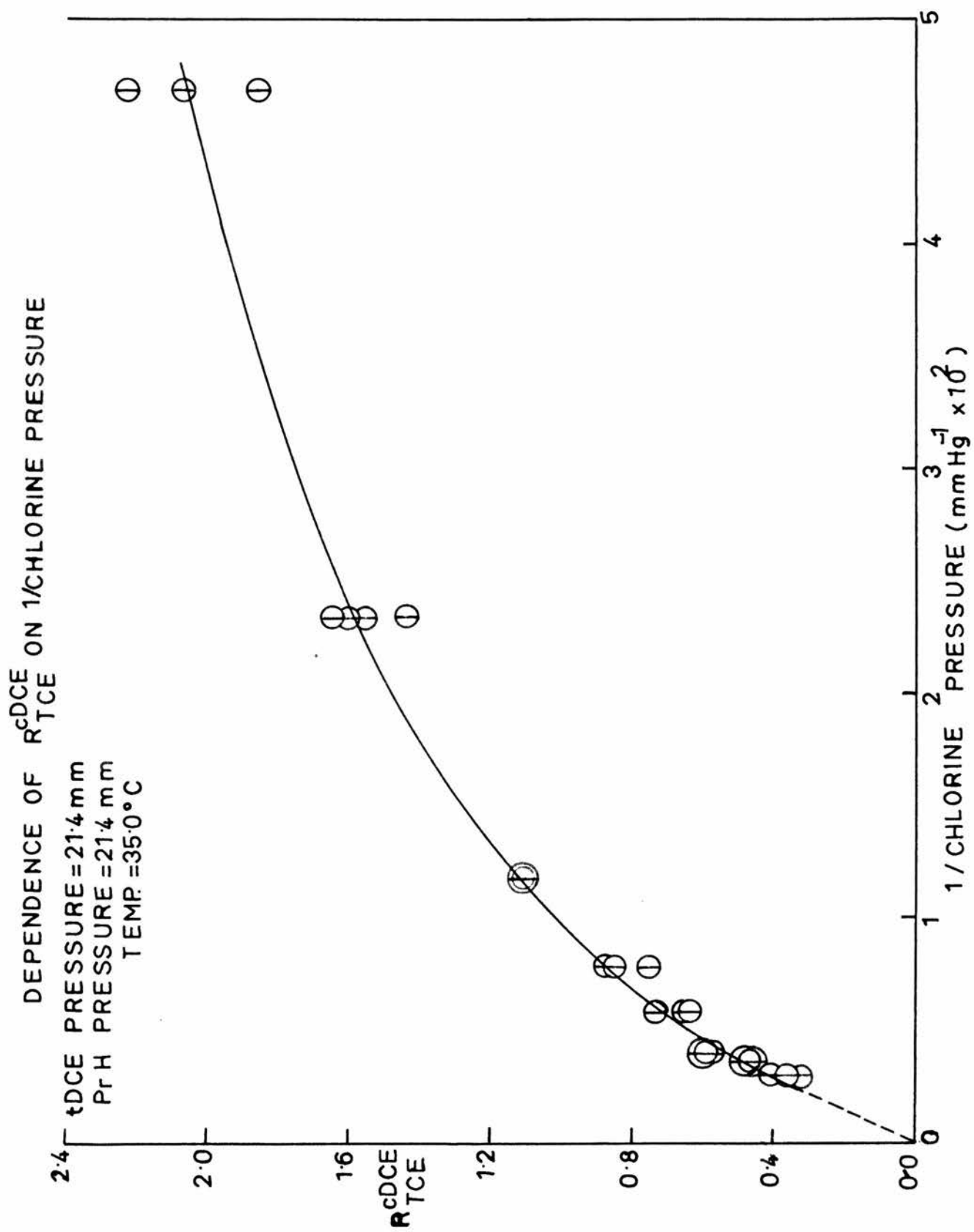
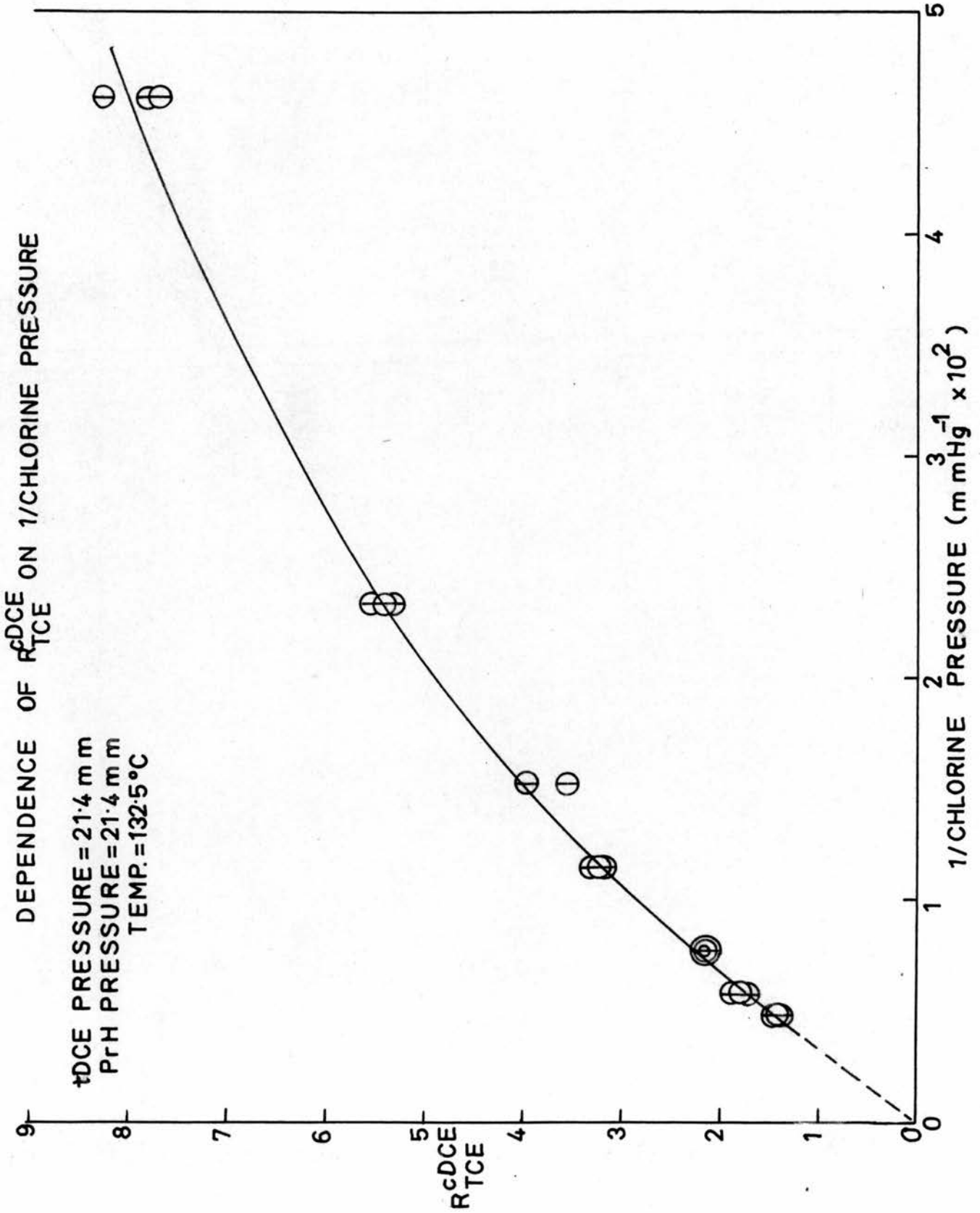


FIG. III.22 a



DEPENDENCE OF R_{tDCE}^{nPrCl} AND R_{tDCE}^{TCE} ON
PROPANE + CIS DICHLOROETHYLENE PRESSURE

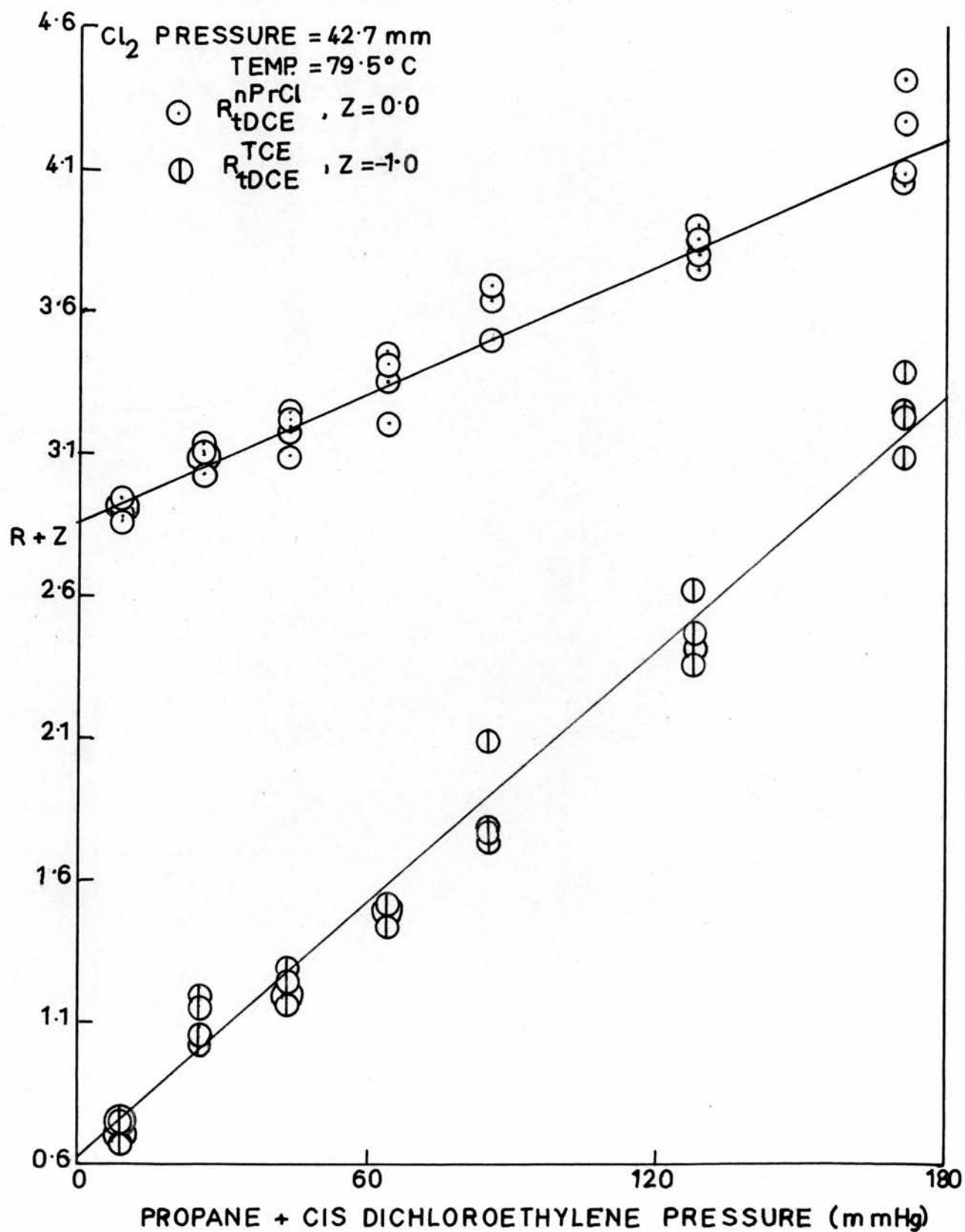


FIG. III.4b

DEPENDENCE OF R_{tDCE}^{nPrCl} AND R_{tDCE}^{TCE} ON
CIS DICHLOROETHYLENE PRESSURE

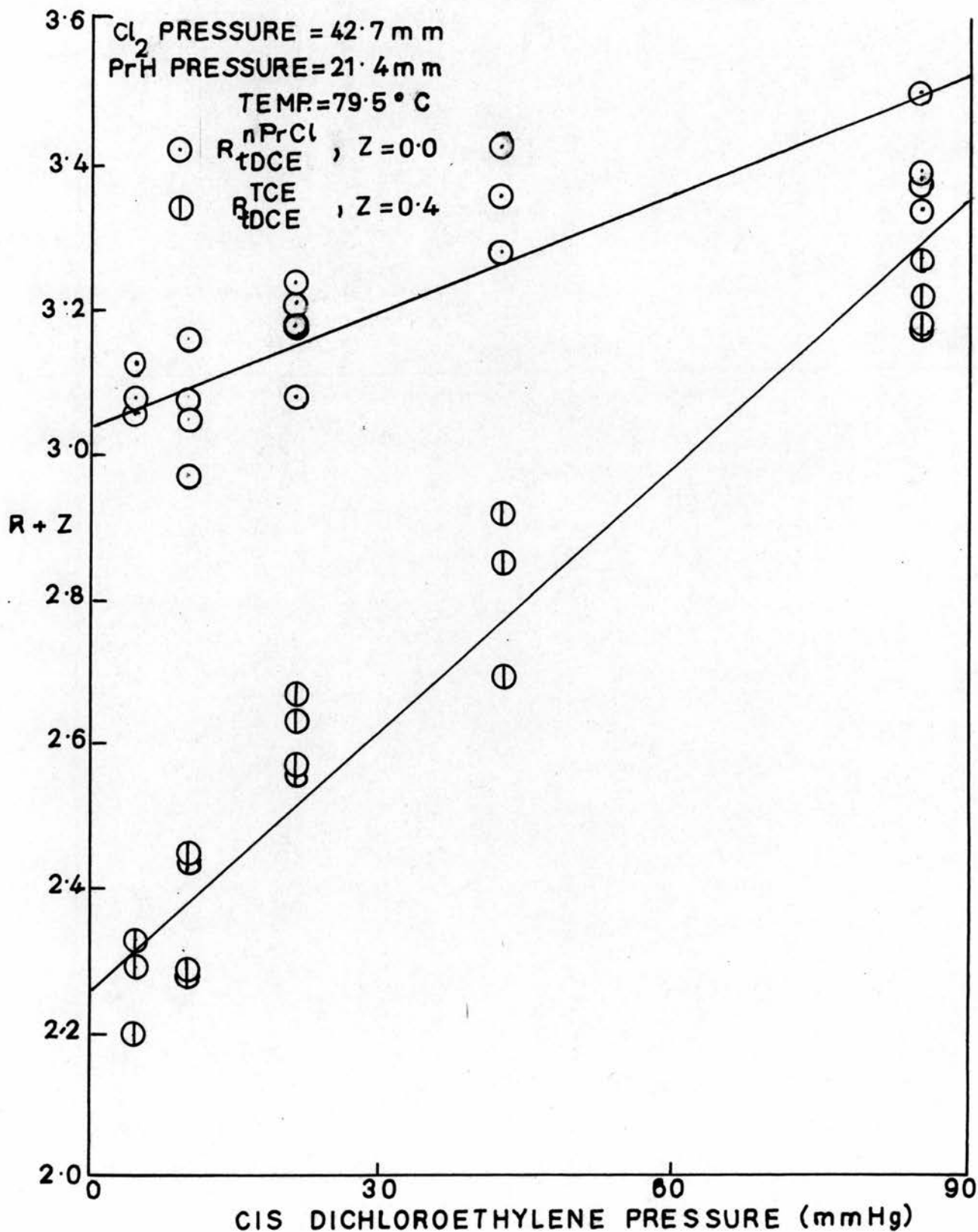


FIG. III. 5b

DEPENDENCE OF R_{tDCE}^{nPrCl} AND R_{tDCE}^{TCE} ON
PROPANE PRESSURE

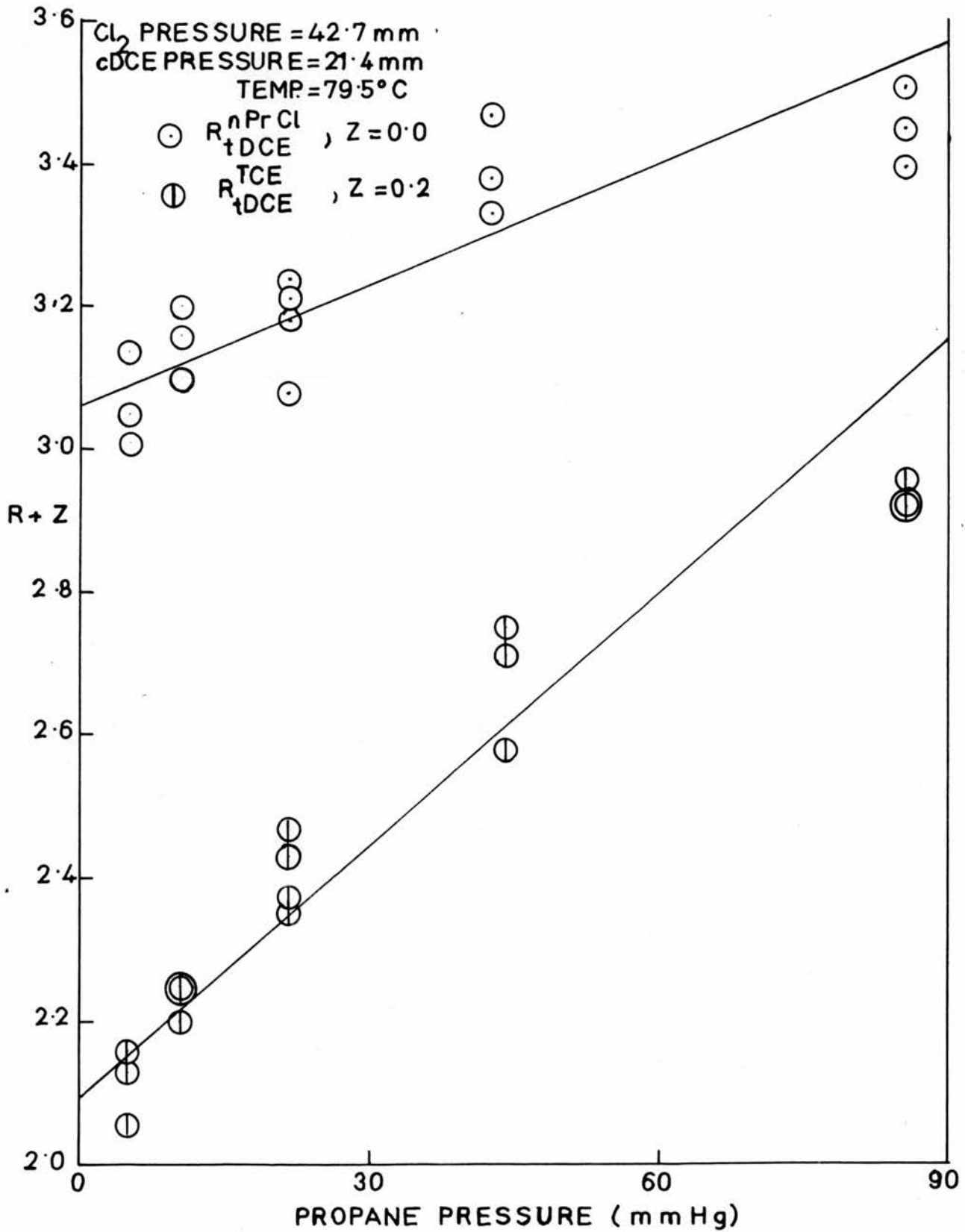


FIG. III.6b

DEPENDENCE OF R_{tDCE}^{nPrCl} AND R_{tDCE}^{TCE} ON CHLORINE PRESSURE

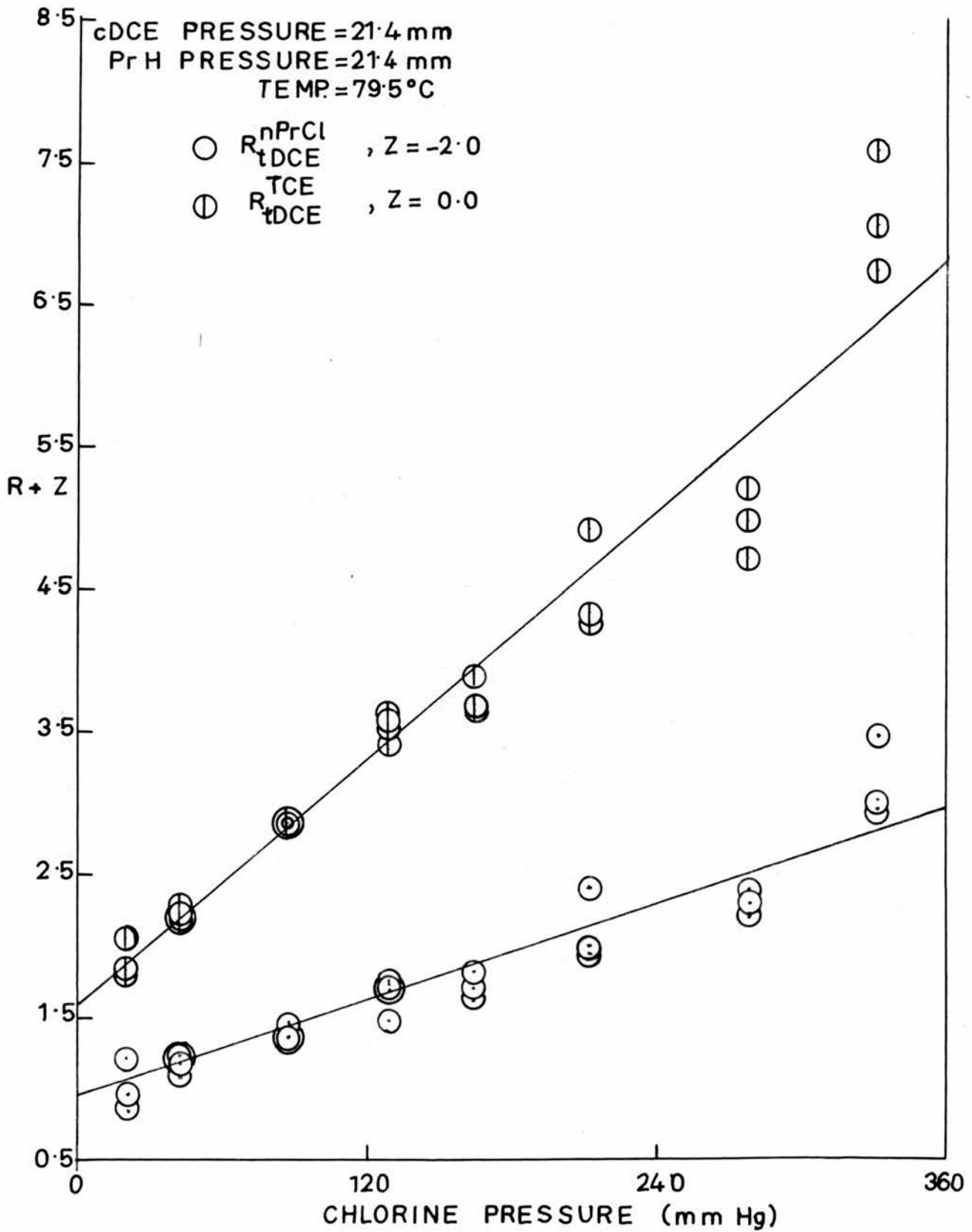
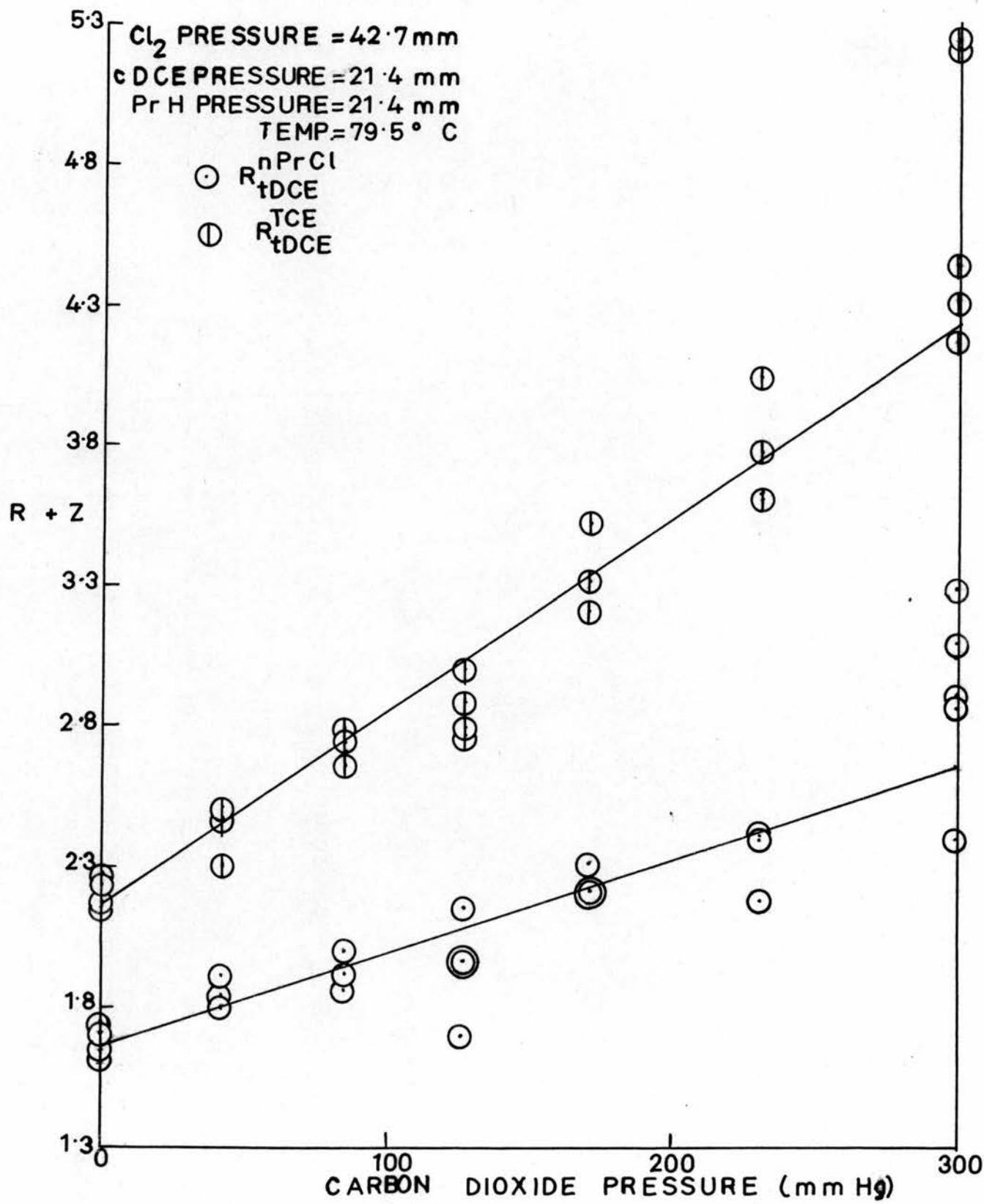


FIG. III.7 b

DEPENDENCE OF R_{tDCE}^{nPrCl} AND R_{tDCE}^{TCE} ON
CARBON DIOXIDE PRESSURE



DEPENDENCE OF R_{cDCE}^{nPrCl} AND R_{cDCE}^{TCE} ON
 PROPANE + TRANS DICHLOROETHYLENE PRESSURE

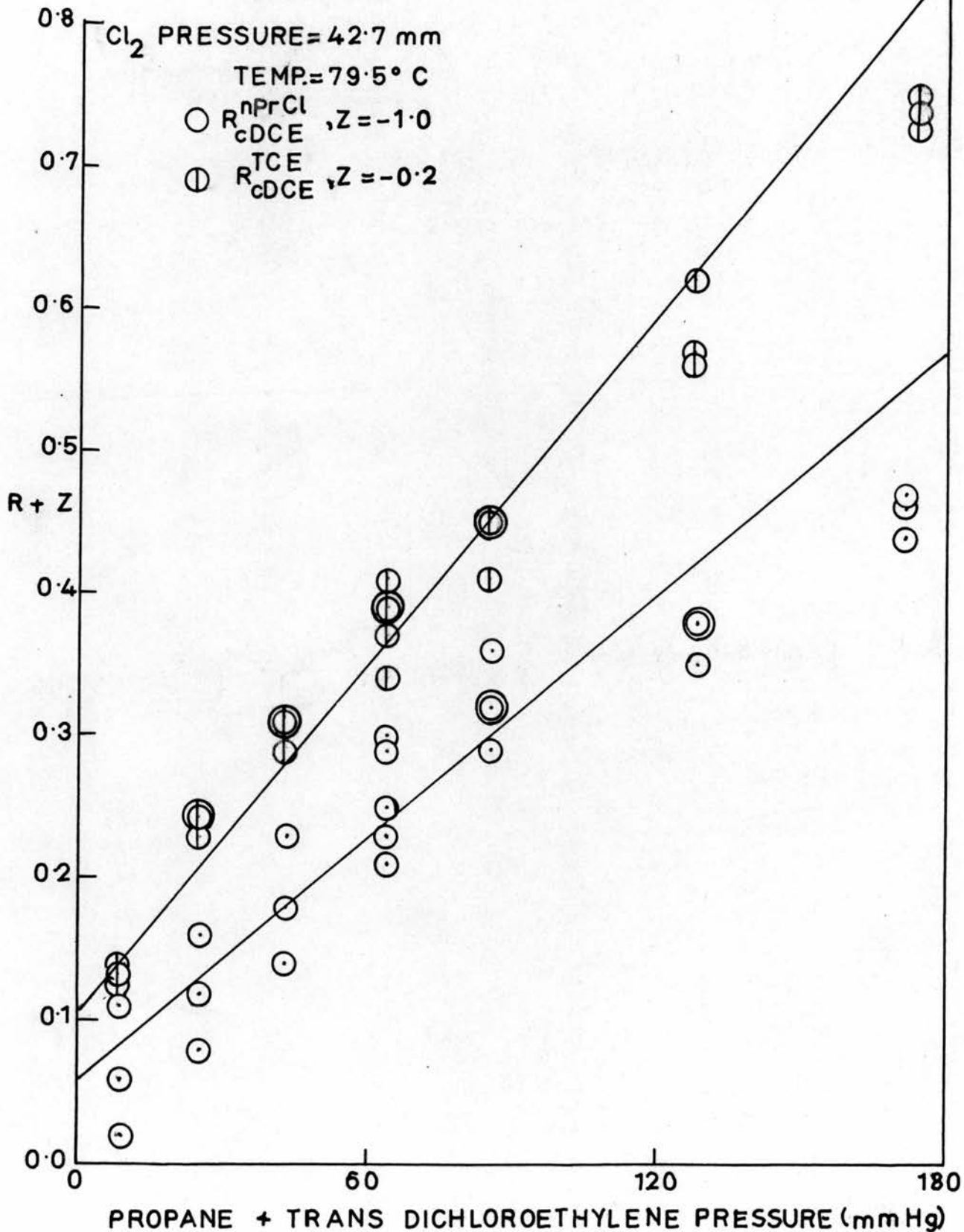
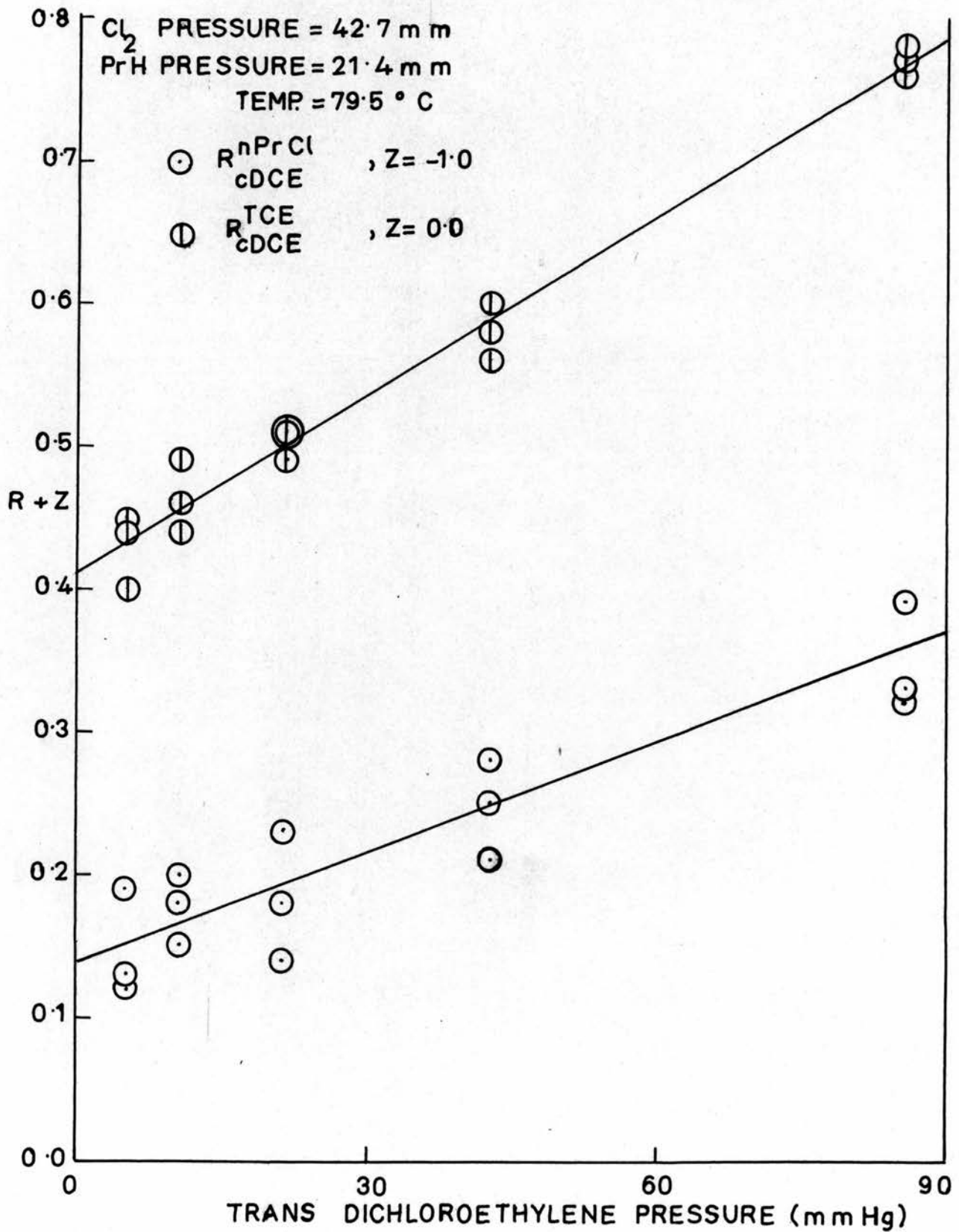


FIG. III.12b

DEPENDENCE OF R_{cDCE}^{nPrCl} AND R_{cDCE}^{TCE} ON
TRANS DICHLOROETHYLENE PRESSURE



DEPENDENCE OF R_{cDCE}^{nPrCl} AND R_{cDCE}^{TCE} ON
PROPANE PRESSURE

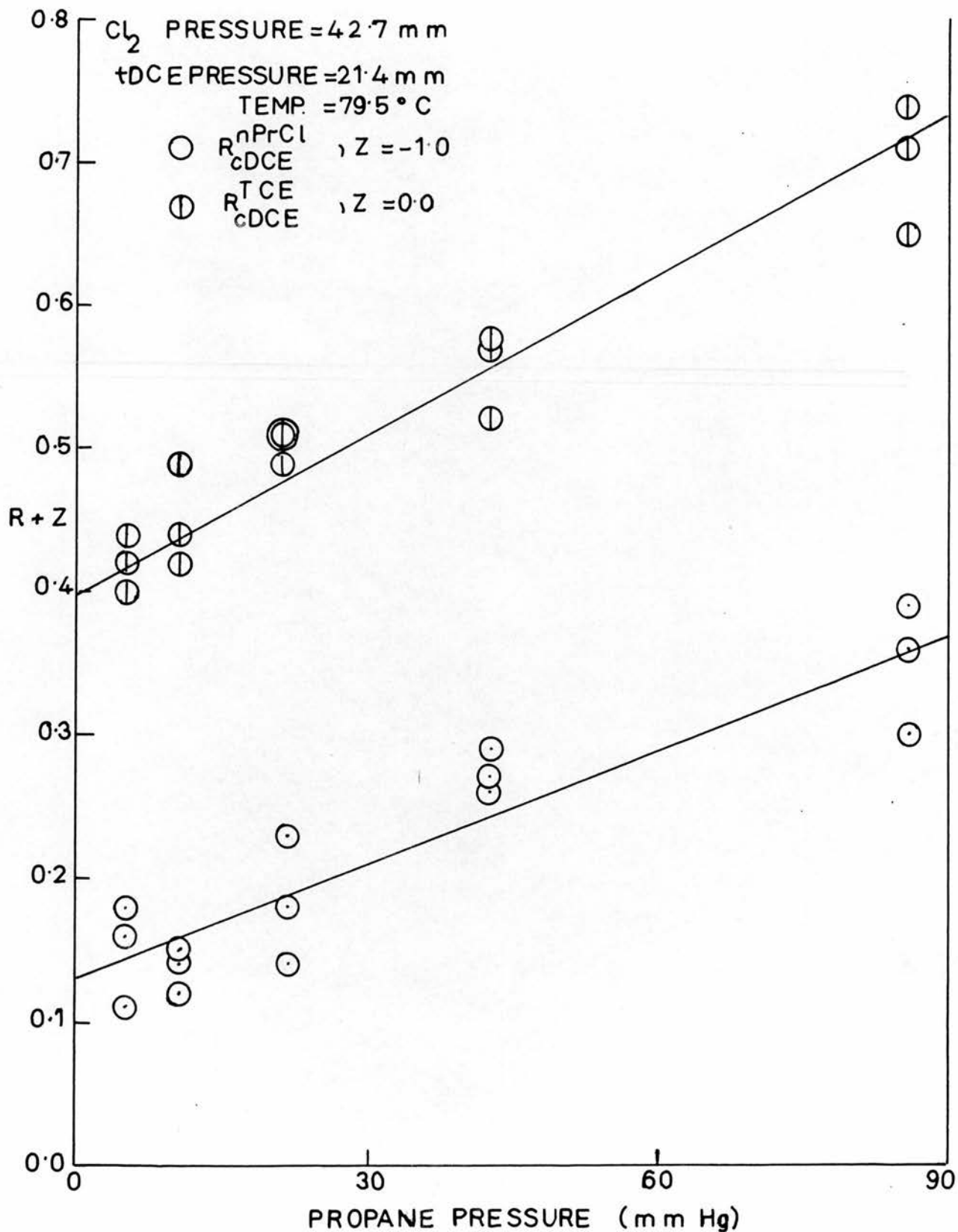


FIG. III.14 b

DEPENDENCE OF R_{cDCE}^{nPrCl} AND R_{cDCE}^{TCE} ON
CHLORINE PRESSURE

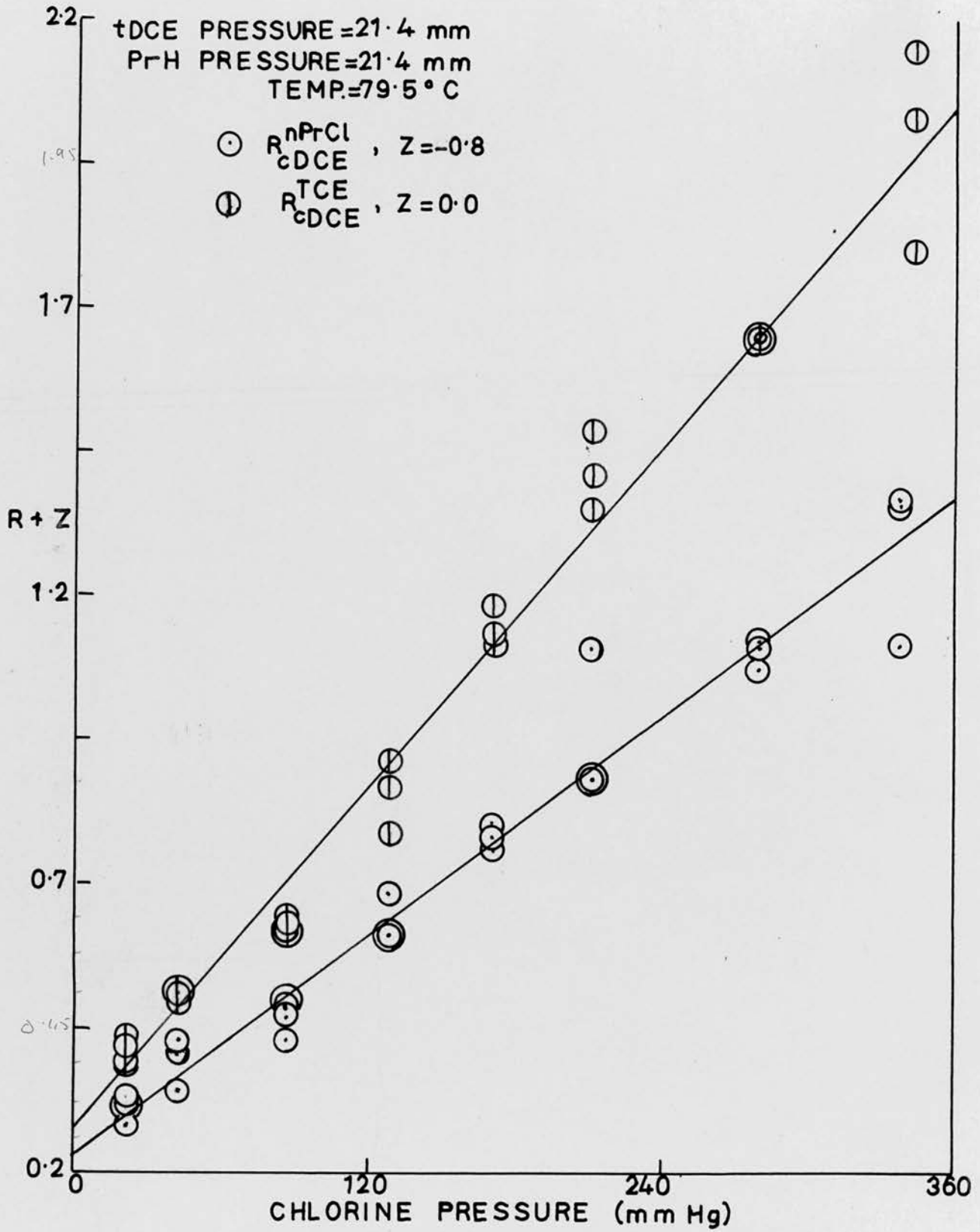


FIG. III.15 b

DEPENDENCE OF R_{cDCE}^{nPrCl} AND R_{cDCE}^{TCE} ON
CARBON DIOXIDE PRESSURE

Cl_2 PRESSURE = 42.7 mm

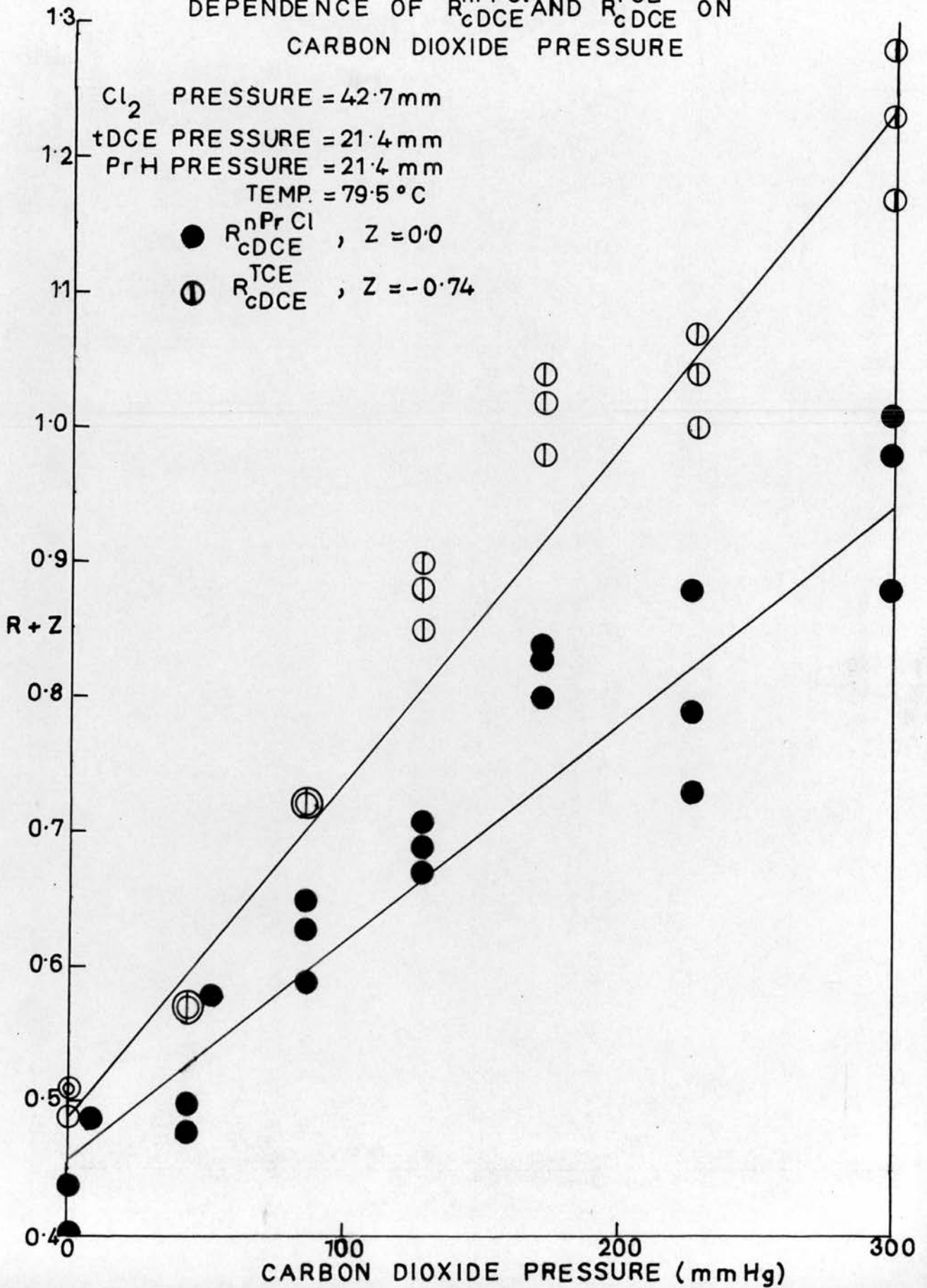
tDCE PRESSURE = 21.4 mm

PrH PRESSURE = 21.4 mm

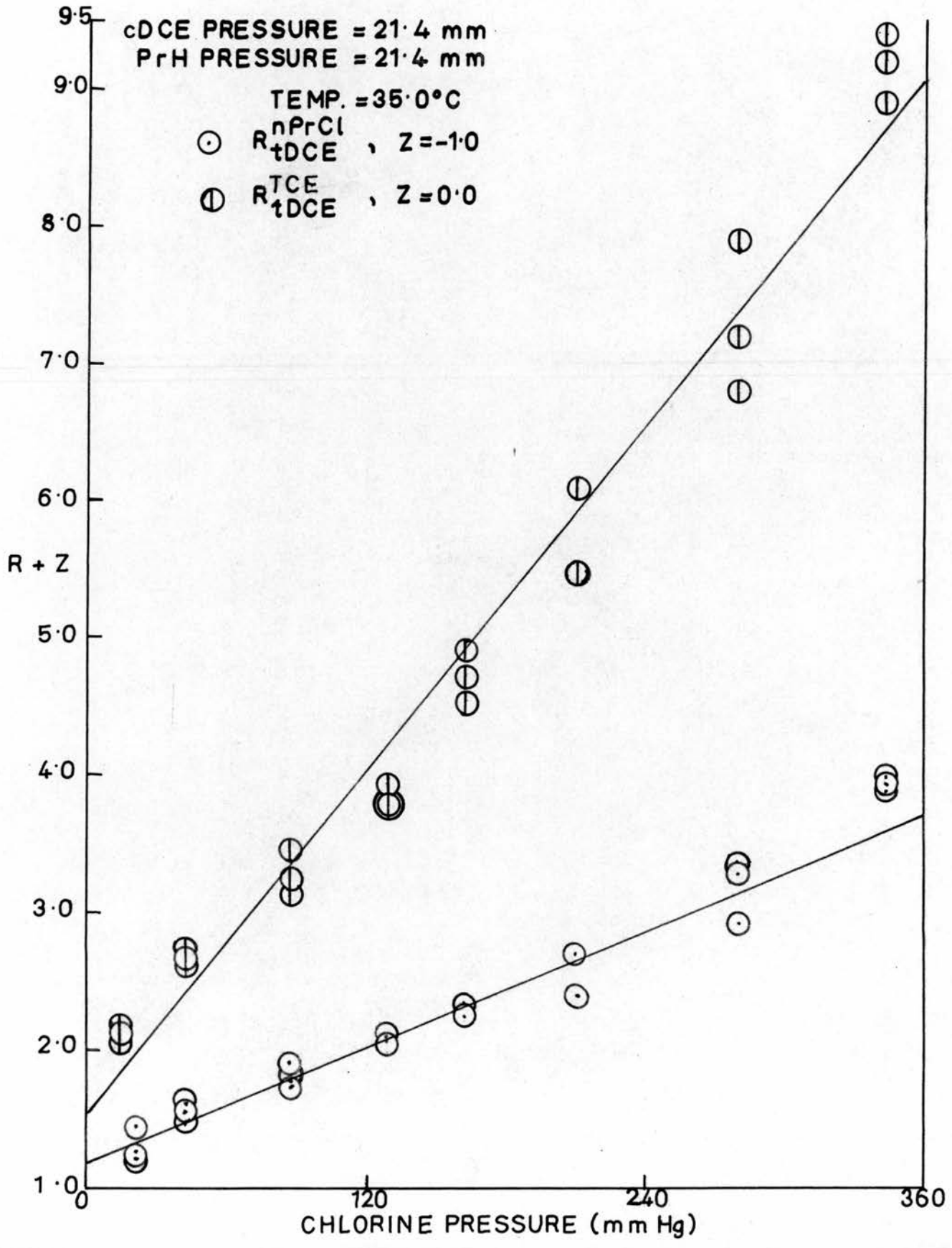
TEMP. = 79.5 °C

● R_{cDCE}^{nPrCl} , Z = 0.0

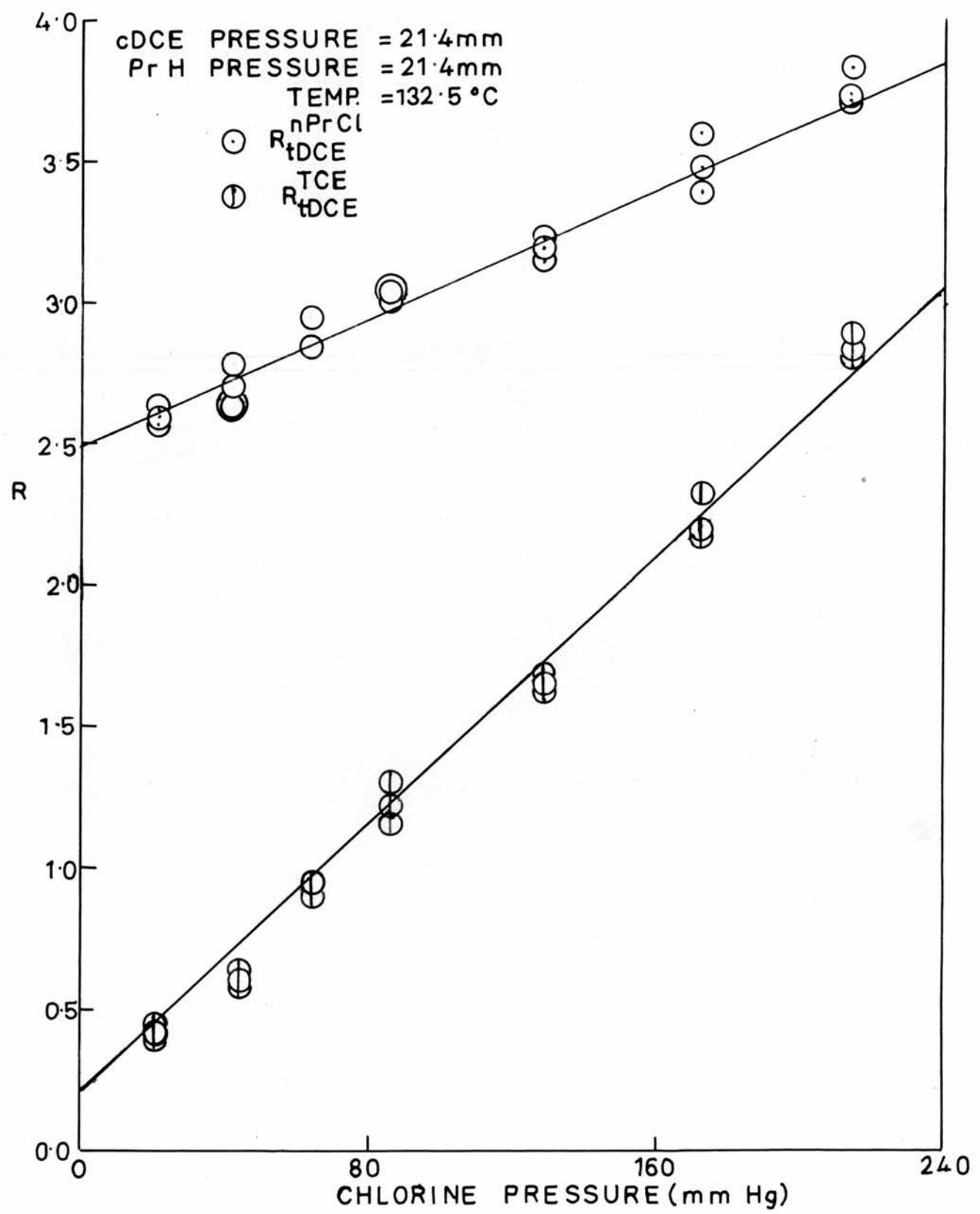
⊙ R_{cDCE}^{TCE} , Z = -0.74



DEPENDENCE OF R_{tDCE}^{nPrCl} AND R_{tDCE}^{TCE} ON
CHLORINE PRESSURE



DEPENDENCE OF R_{tDCE}^{nPrCl} AND R_{tDCE}^{TCE} ON
CHLORINE PRESSURE



DEPENDENCE OF R_{cDCE}^{nPrCl} AND R_{cDCE}^{TCE} ON
CHLORINE PRESSURE

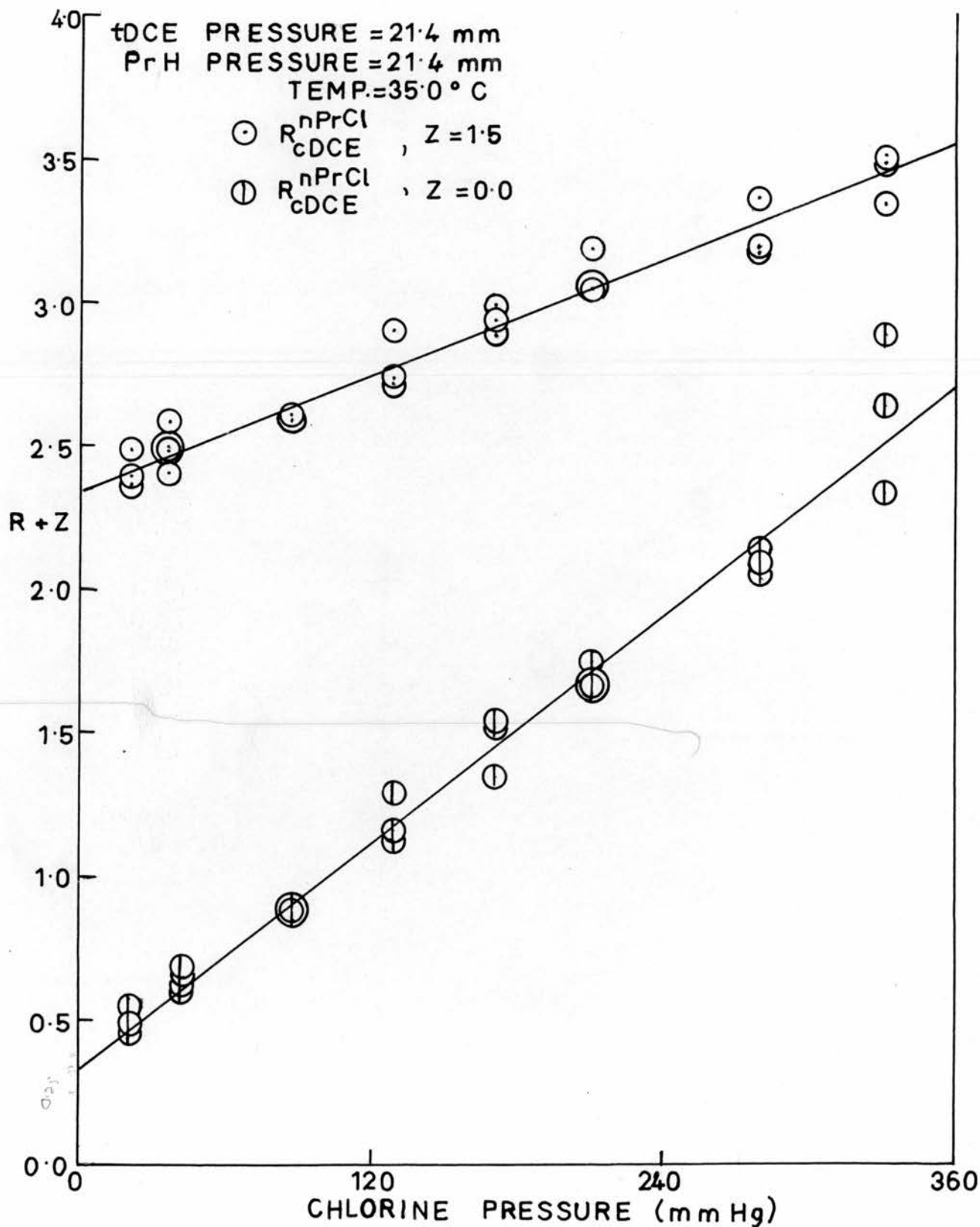


FIG. III. 22 b

DEPENDENCE OF R_{cDCE}^{nPrCl} AND R_{cDCE}^{TCE} ON
CHLORINE PRESSURE

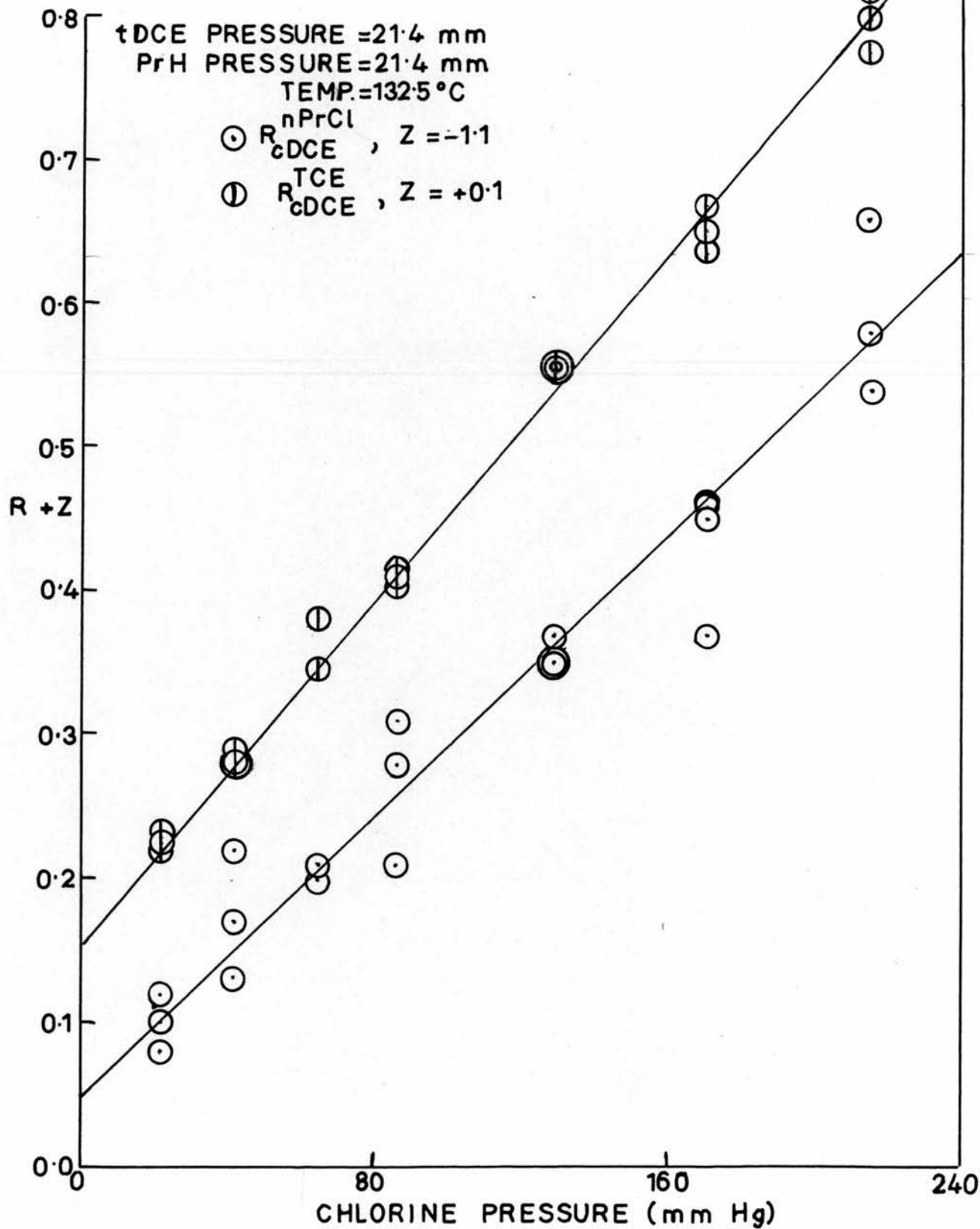


FIG. III.3c

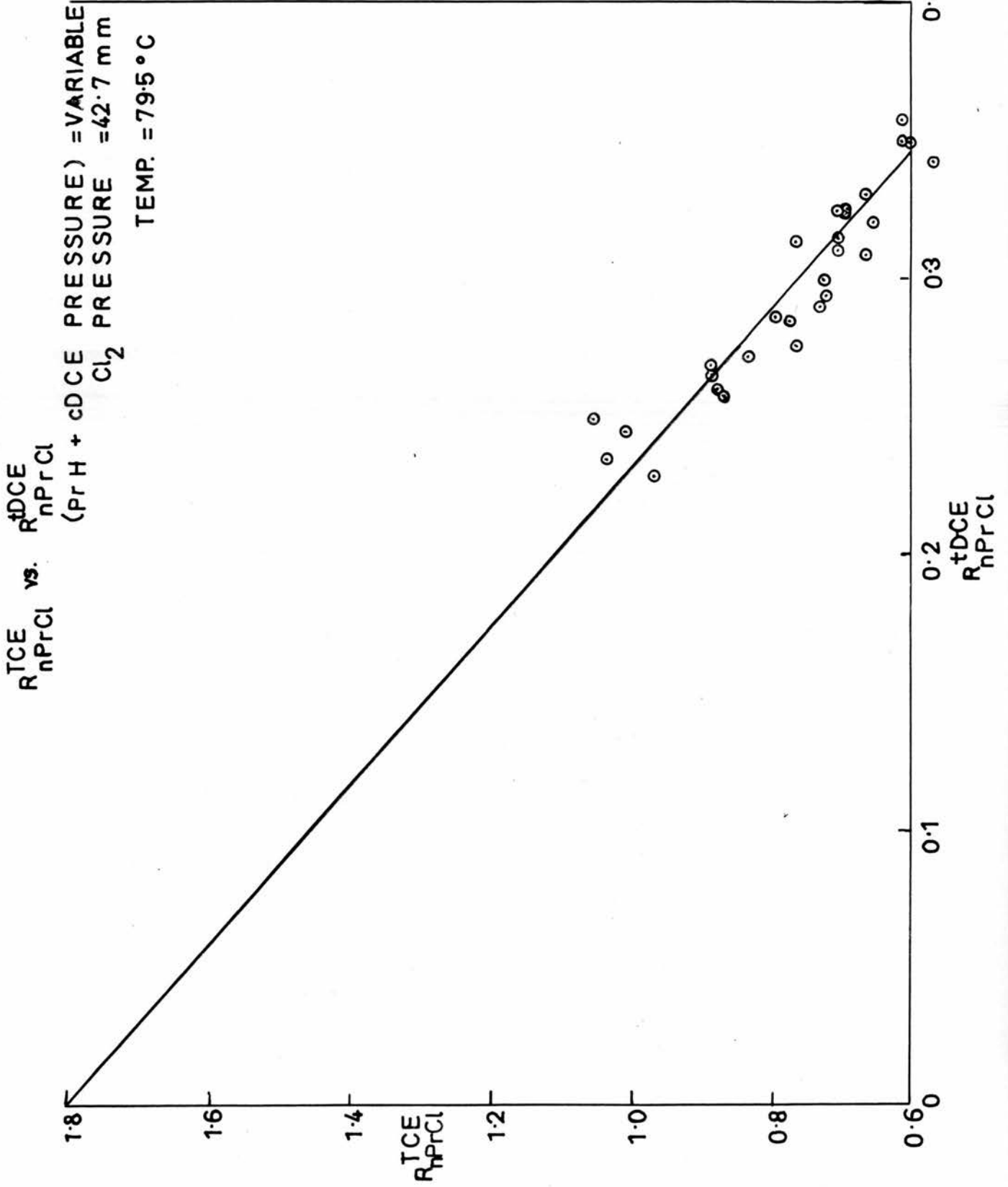


FIG. III 4c

R_{nPrCl}^{TCE} vs. R_{nPrCl}^{tDCE}

cDCE PRESSURE = VARIABLE
PrH PRESSURE = 21.4 mm
Cl₂ PRESSURE = 42.7 mm
TEMP. = 79.5 °C

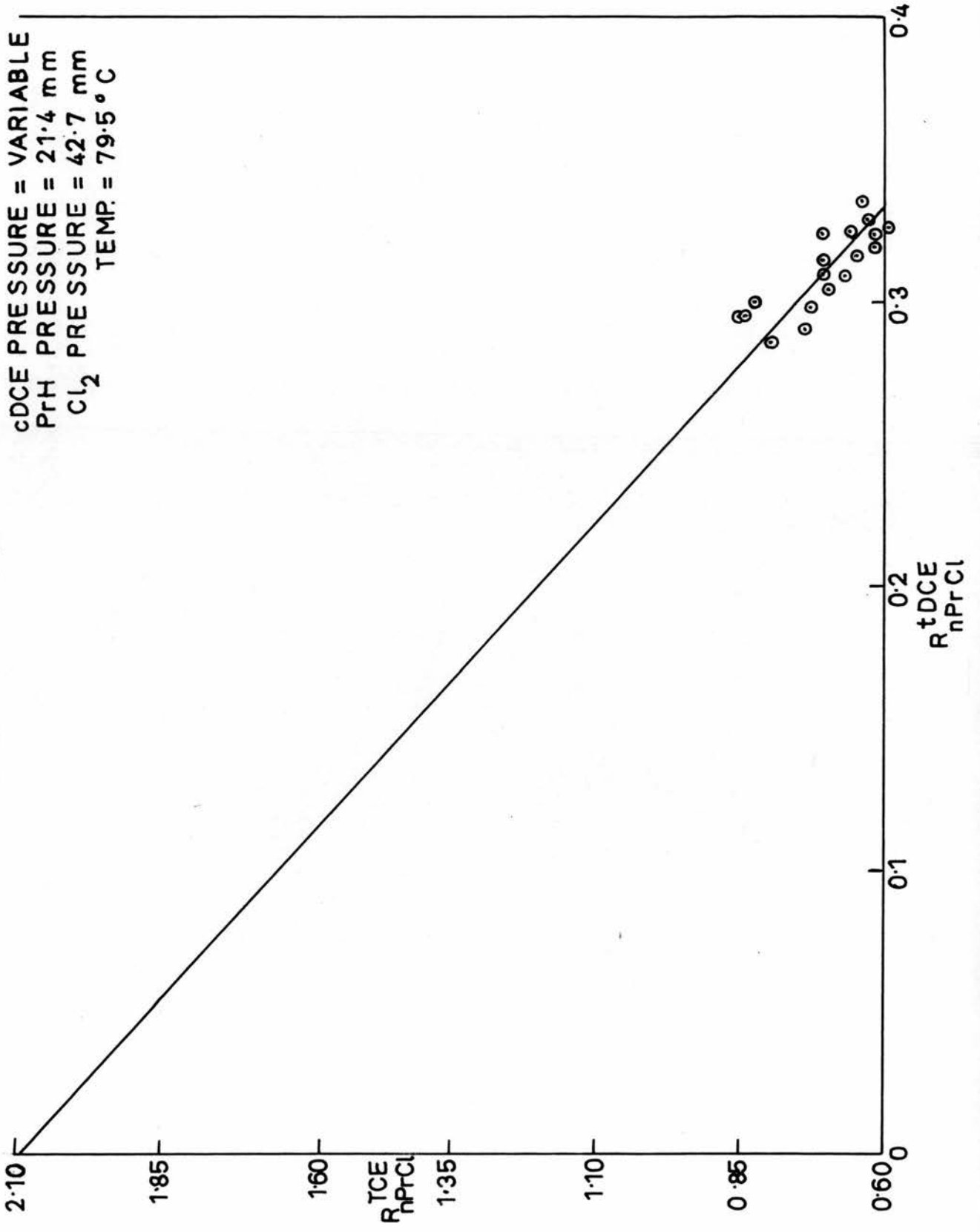


FIG. III.5c

R_{nPrCl}^{TCE} vs. R_{nPrCl}^{tDCE}

PrH PRESSURE = VARIABLE
cDCE PRESSURE = 21.4 mm
Cl₂ PRESSURE = 42.7 mm
TEMP. = 79.5 °C

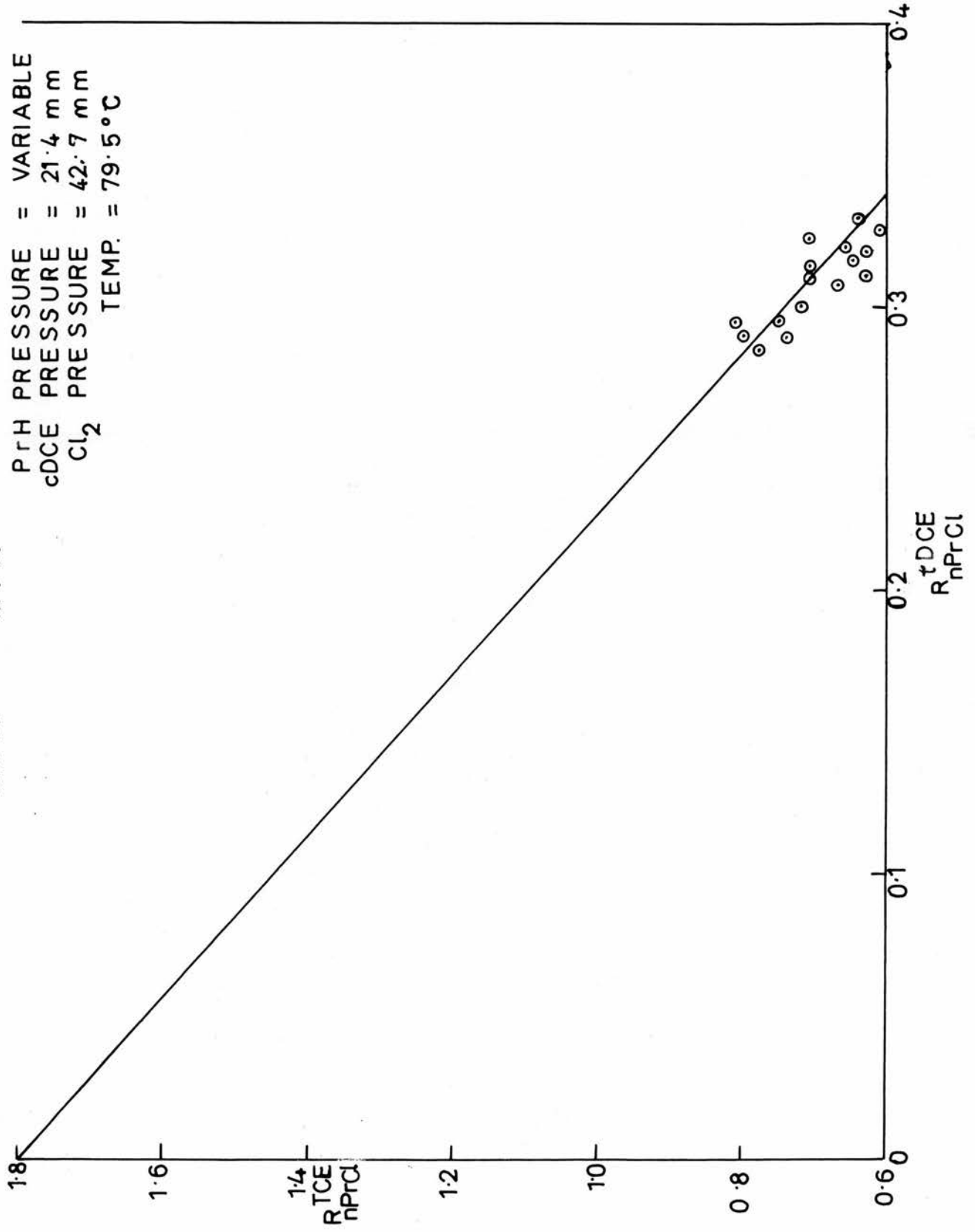


FIG. III.6c

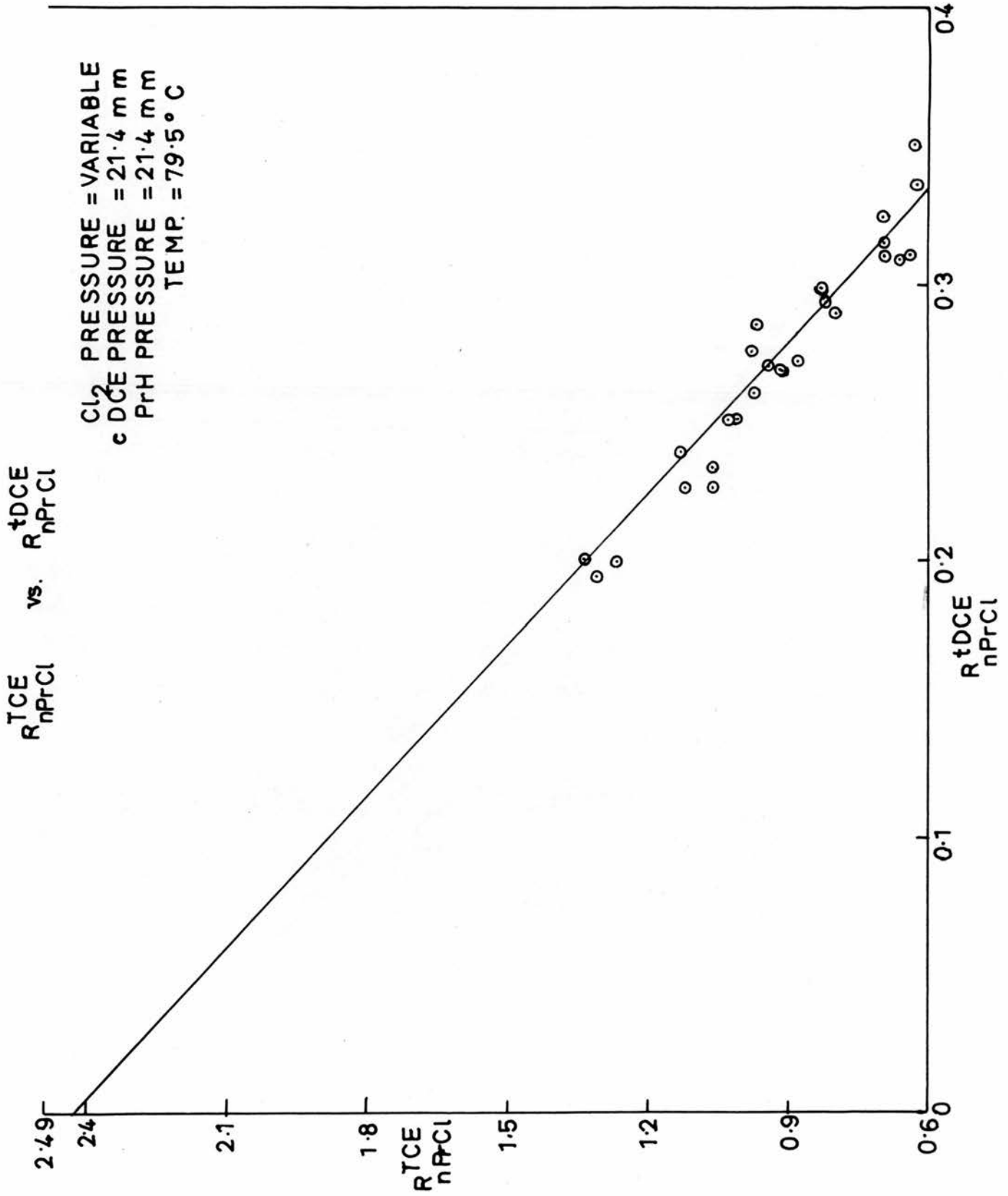


FIG. III.7c

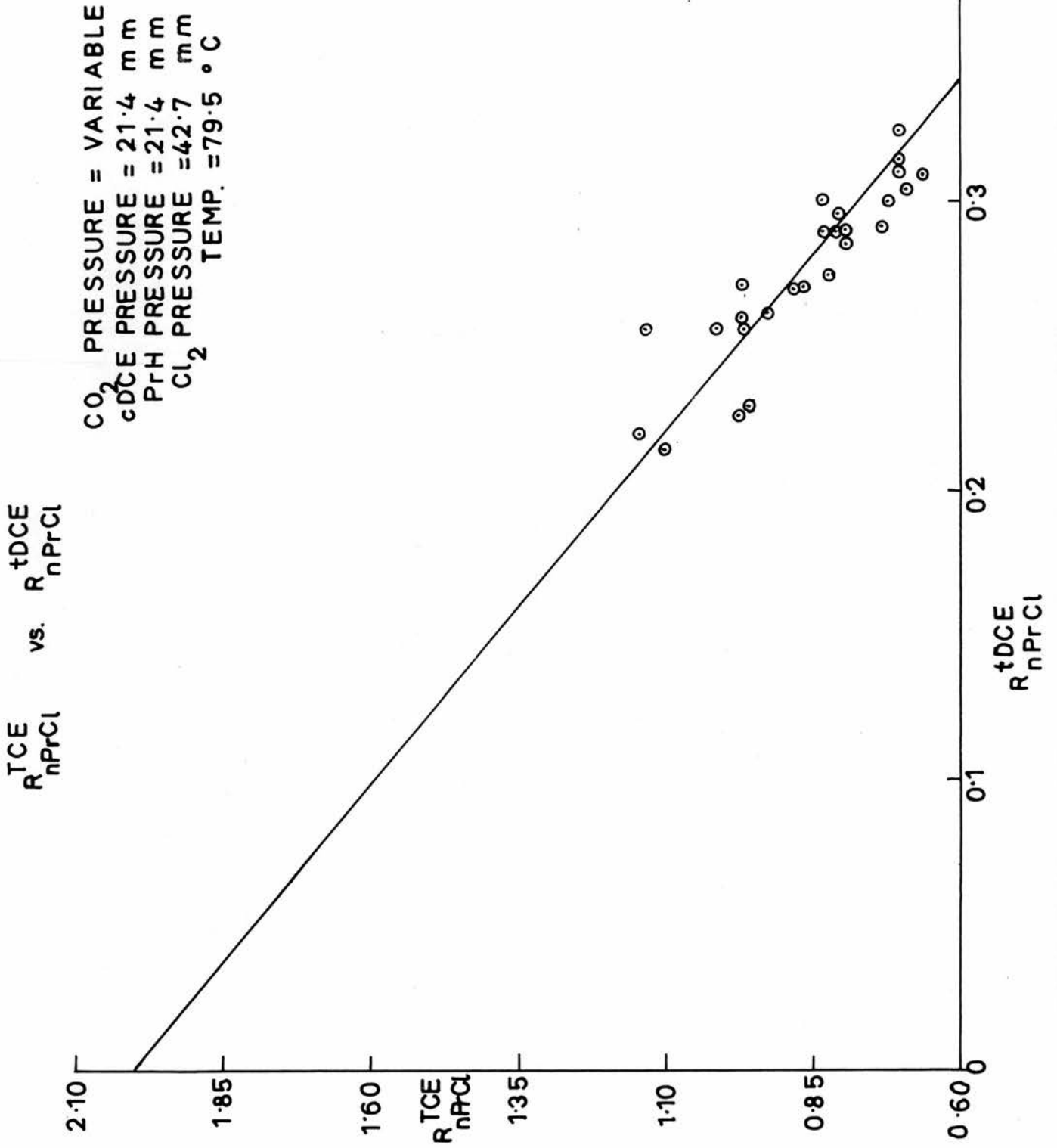


FIG. III.8c

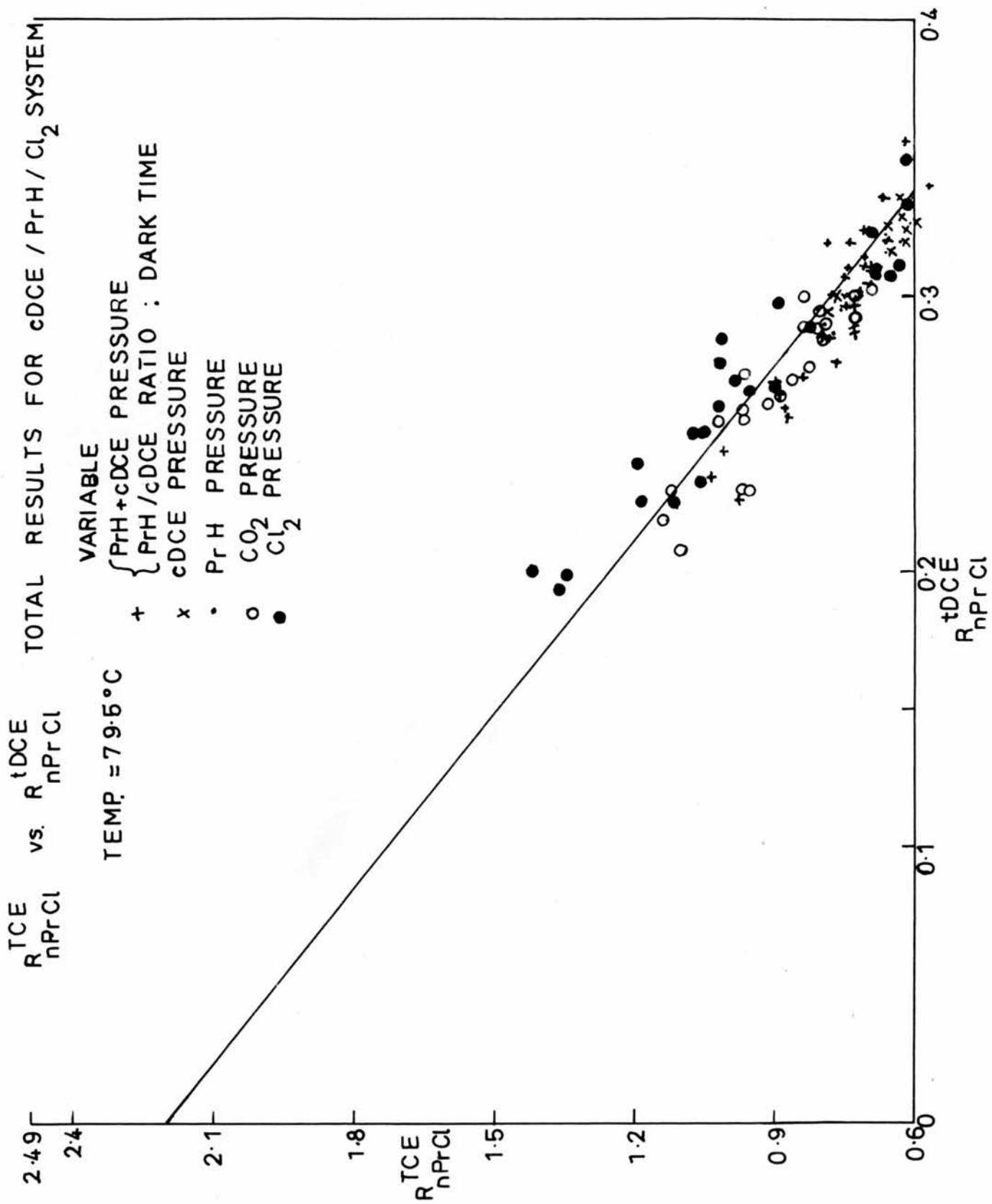


FIG. III .11c

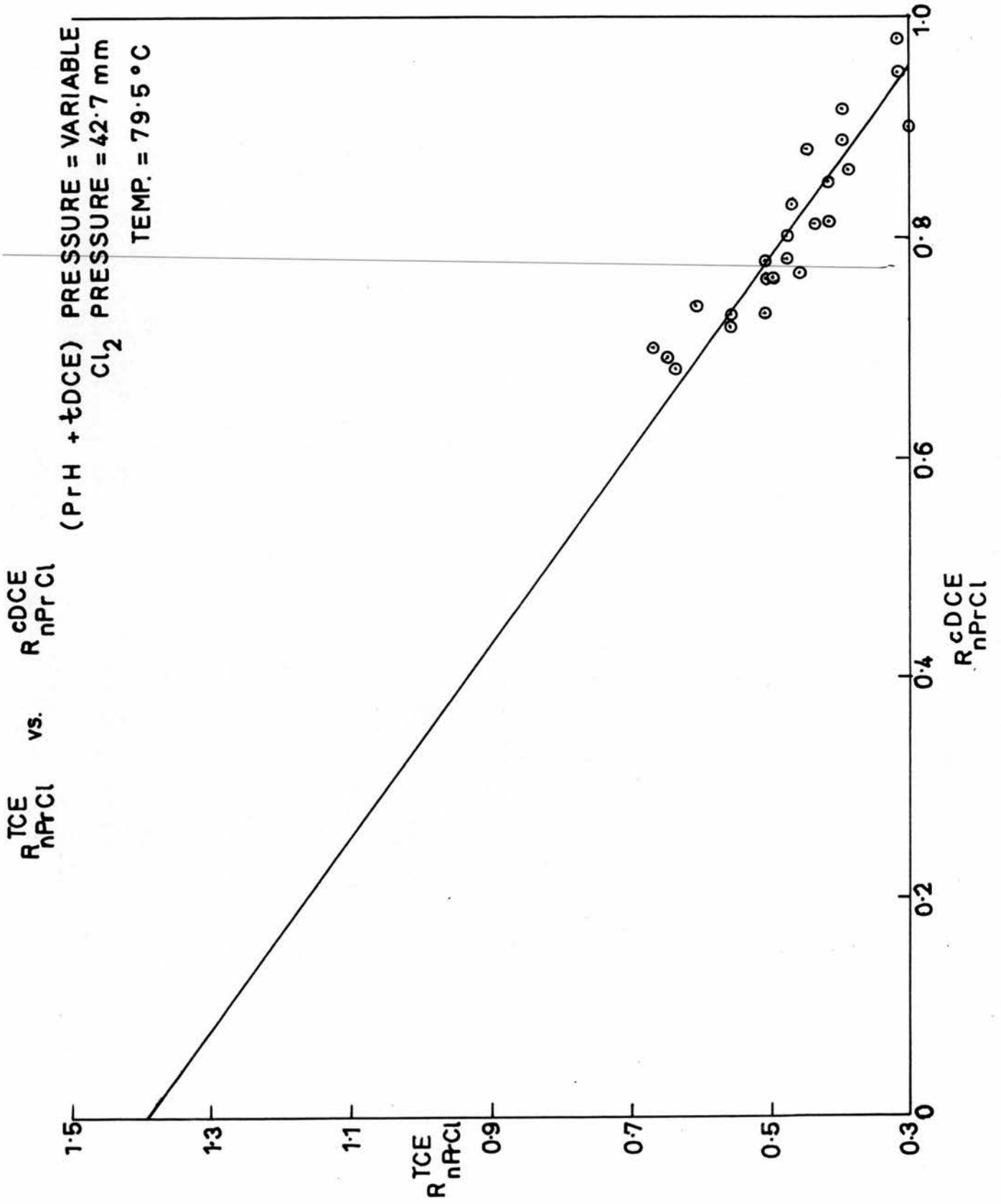


FIG. III, 12c

R_{nPrCl}^{TCE} vs. R_{nPrCl}^{cDCE}
 tDCE PRESSURE = VARIABLE
 PrH PRESSURE = 21.4 mm
 Cl₂ PRESSURE = 42.7 mm
 TEMP = 79.5° C

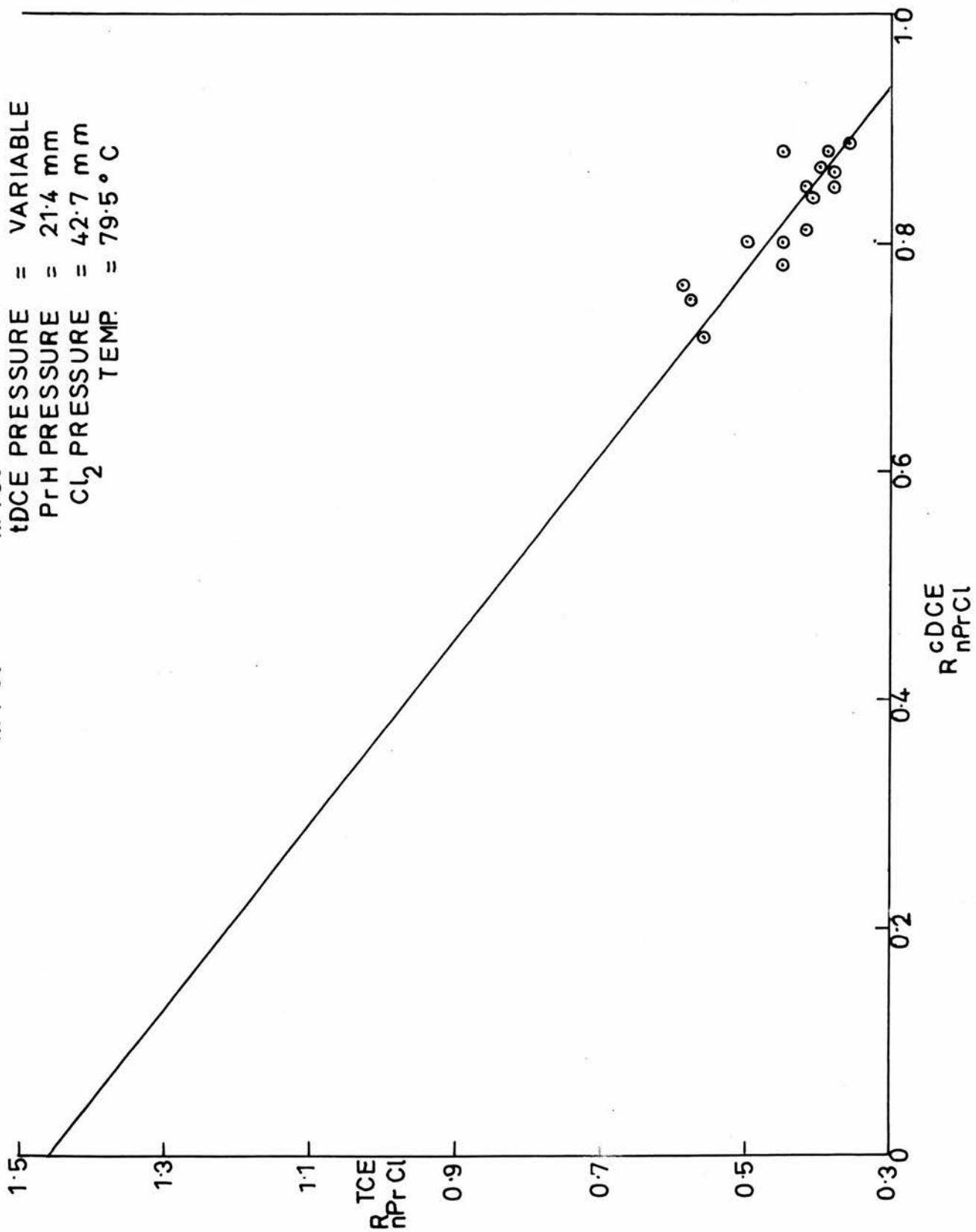


FIG. III.13c

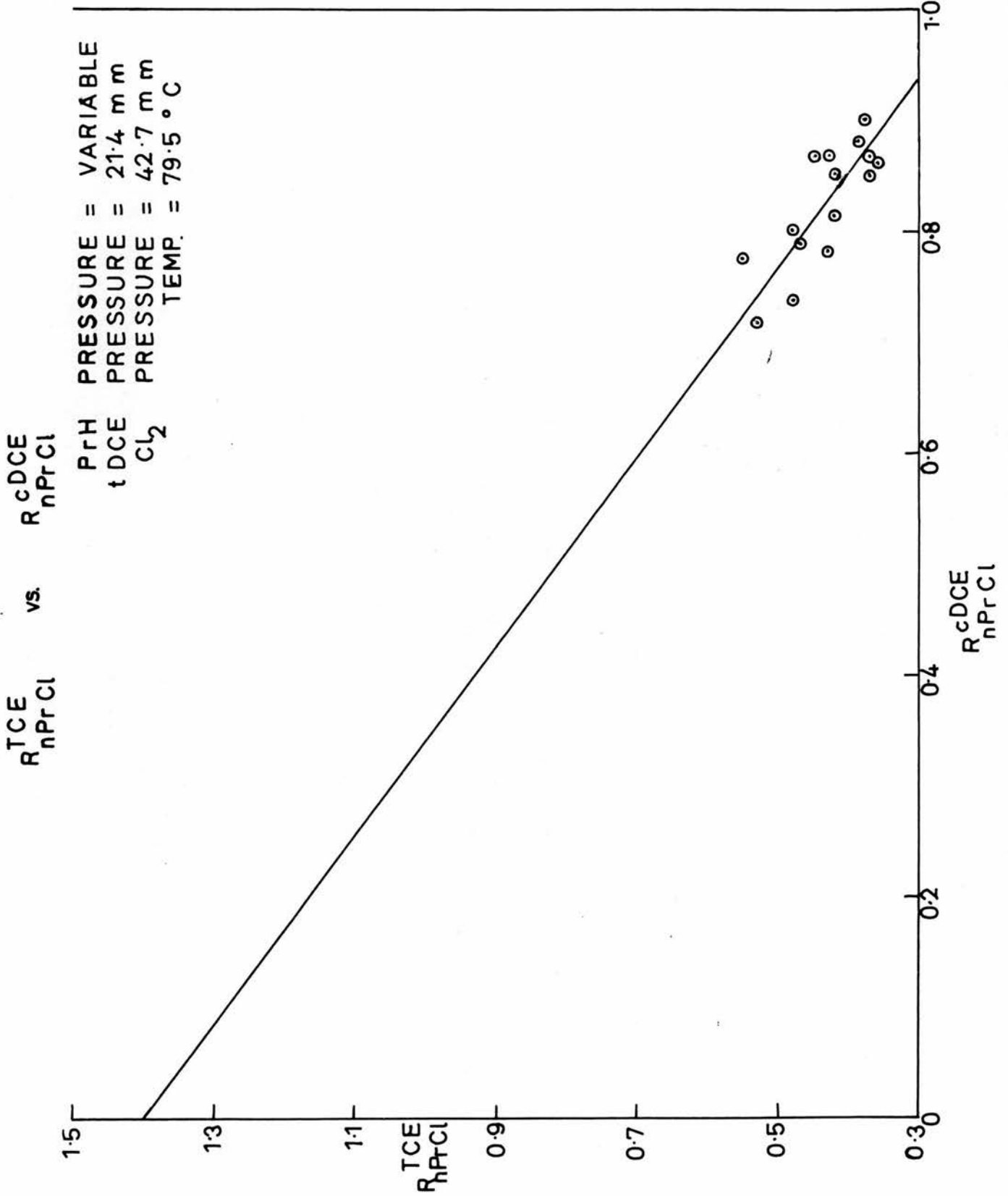


FIG. III.14c

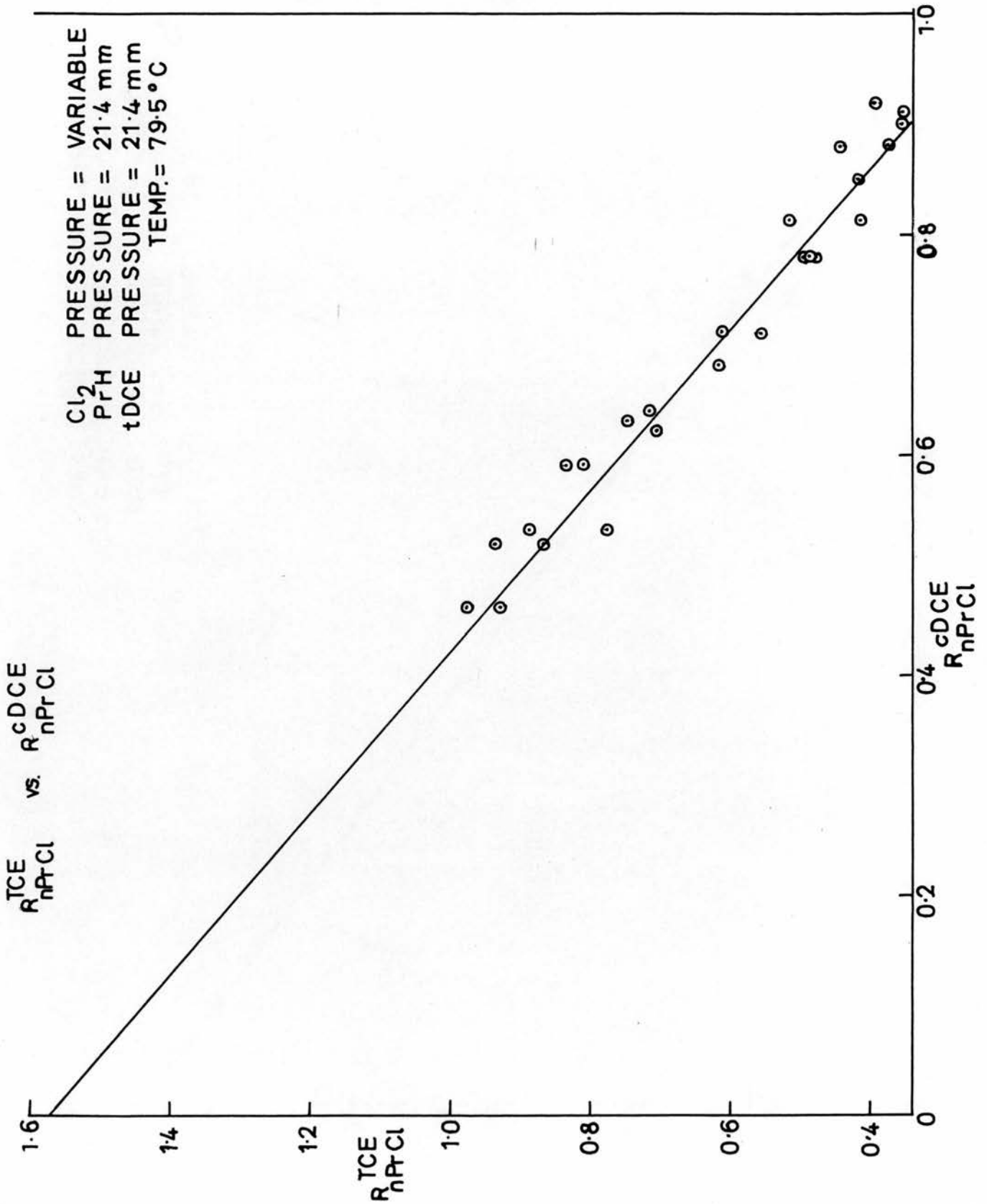


FIG. III.15 c

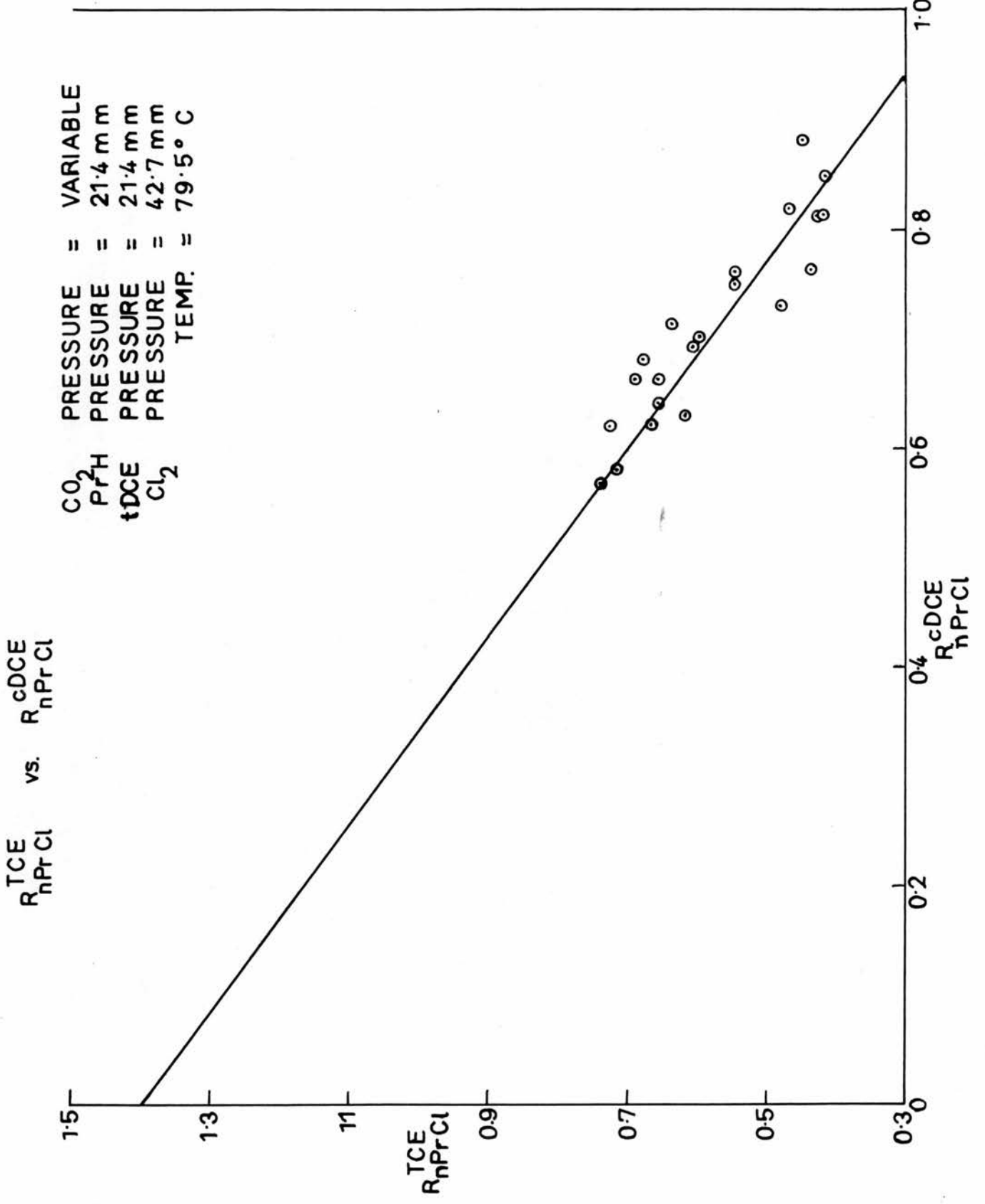


FIG. III.16c

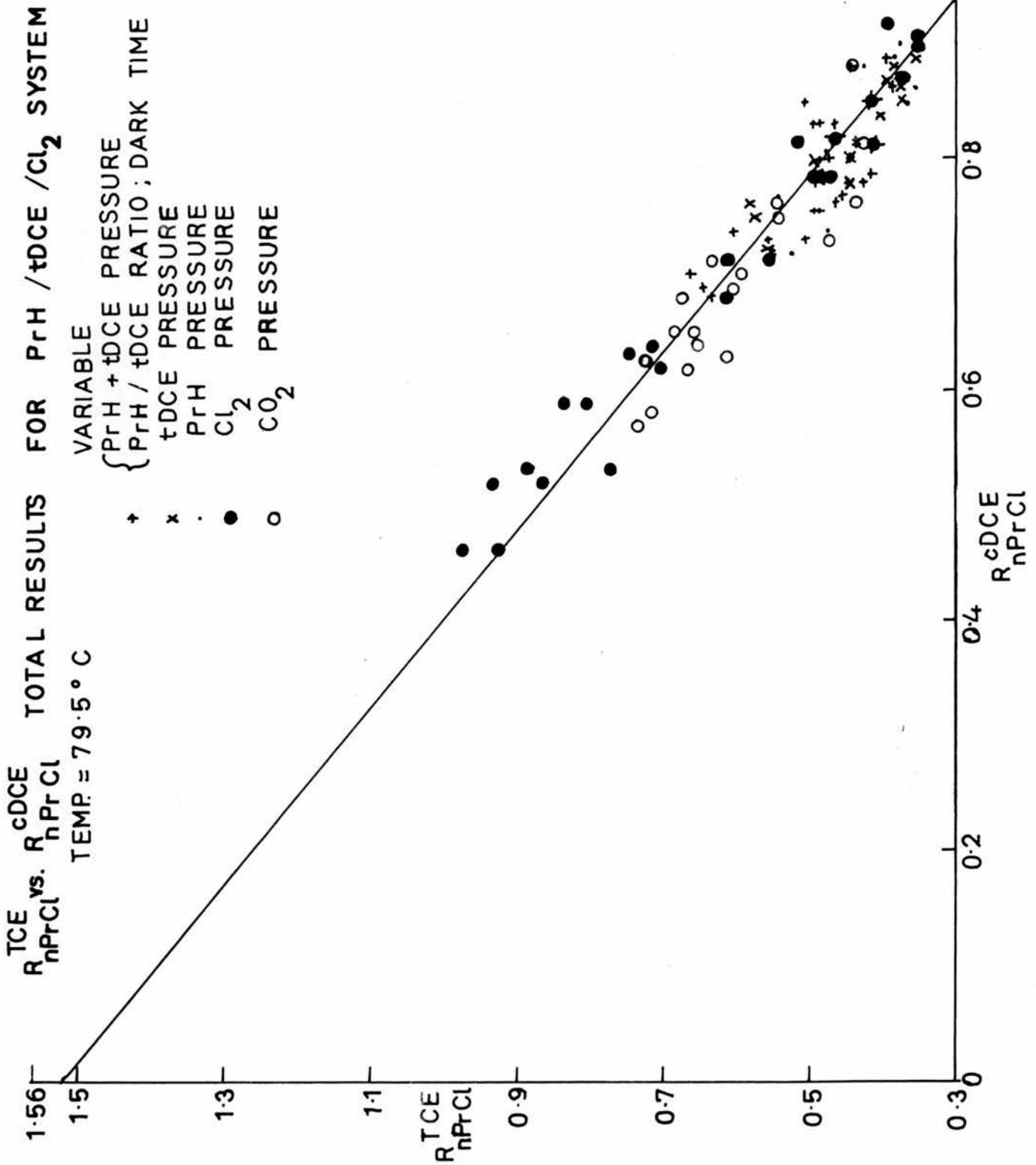


FIG. III .19c

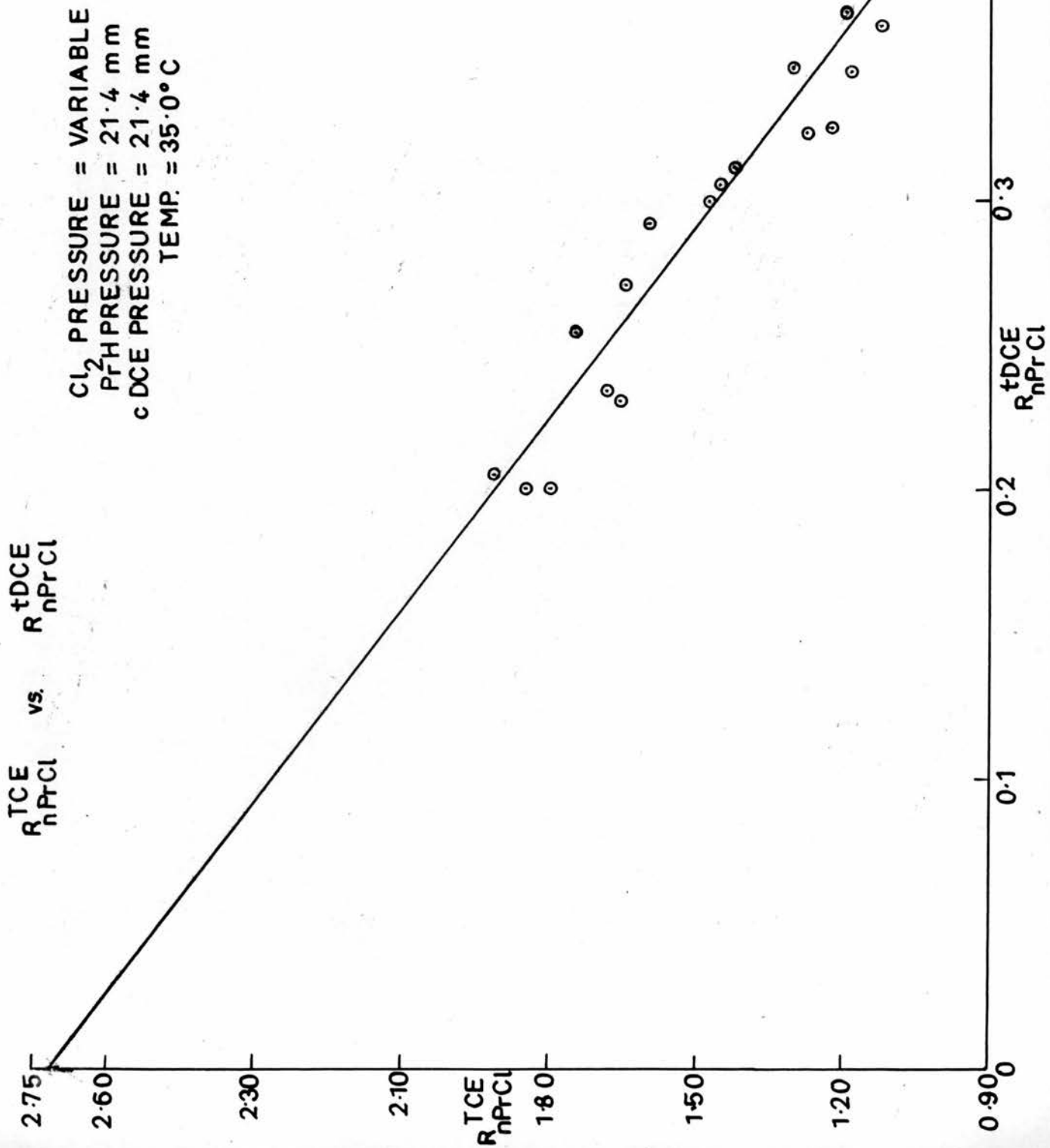


FIG. III.20c

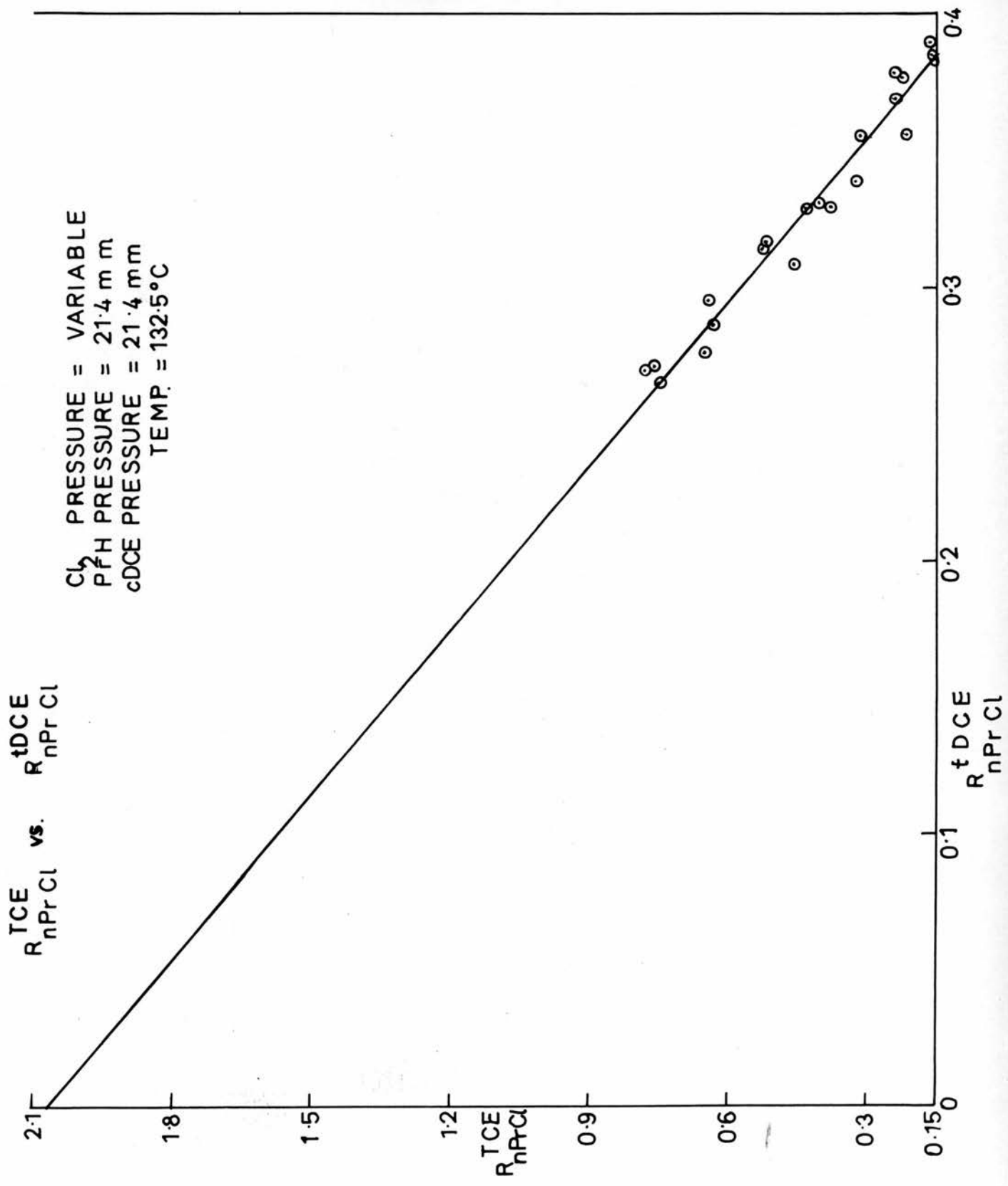


FIG. III.21c

TCE vs. R_{nPrCl}^{cDCE}

Cl_2 PRESSURE = VARIABLE
 PrH PRESSURE = 21.4 mm
 tDCE PRESSURE = 21.4 mm
 TEMP. = 35.0°C

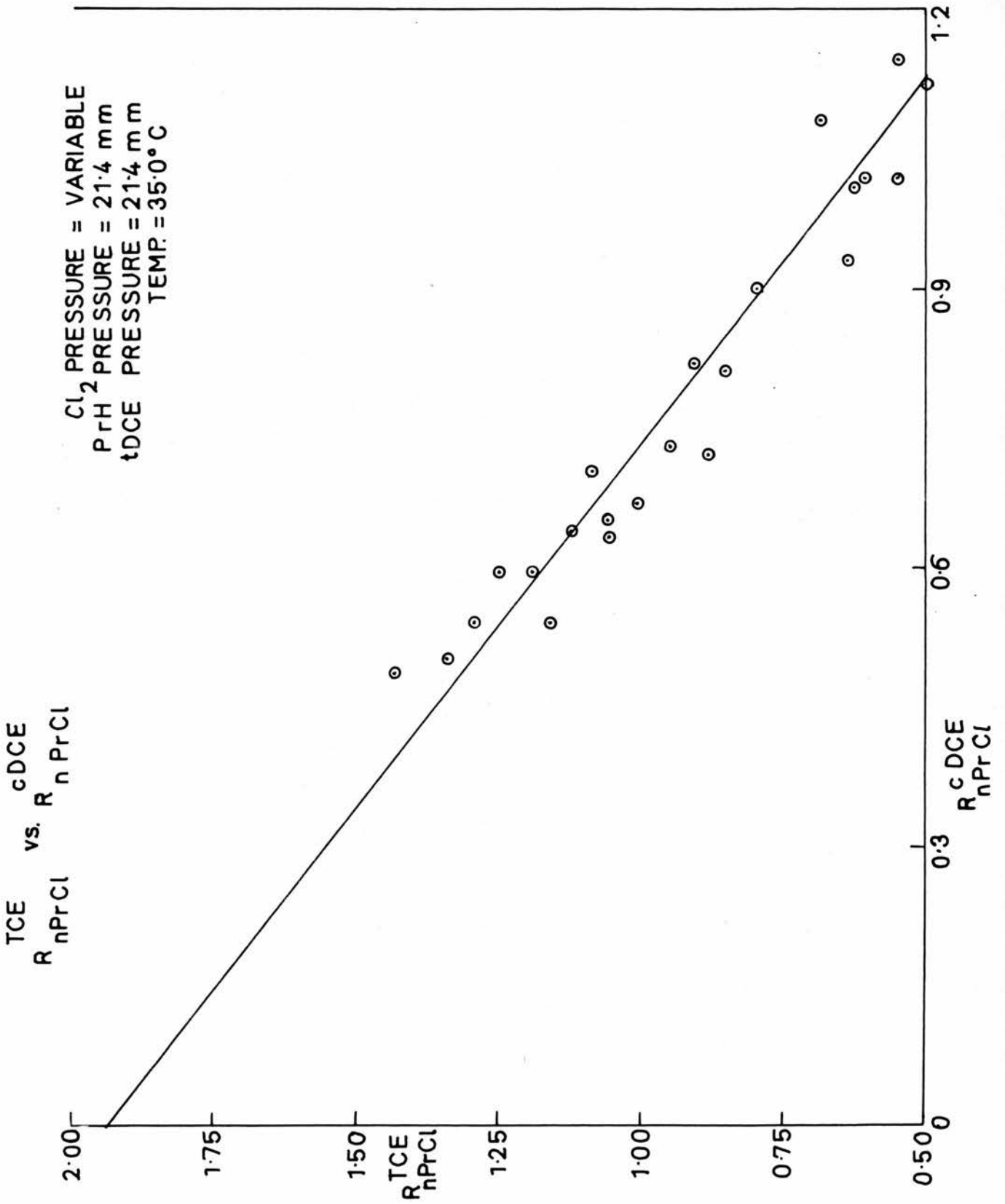
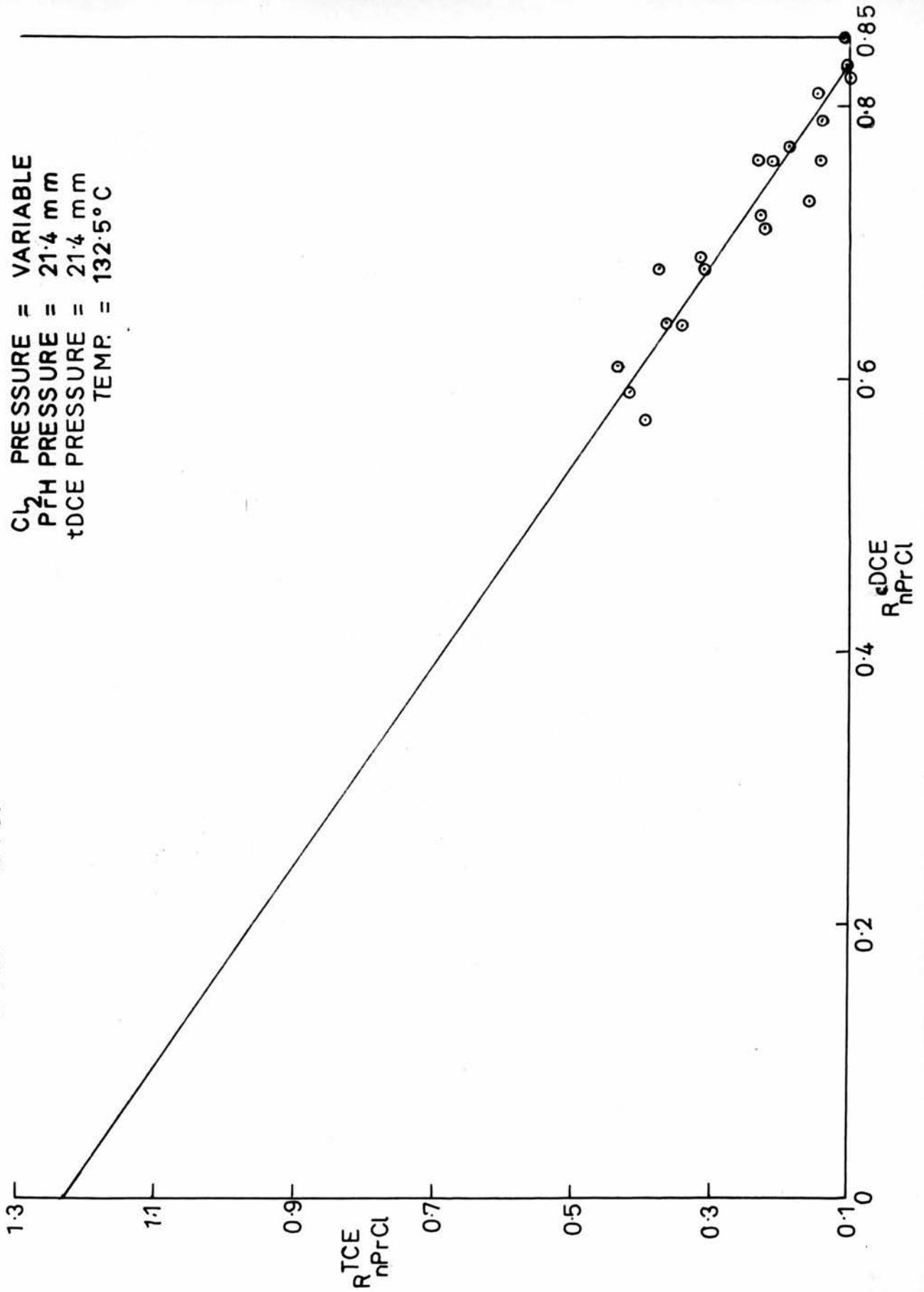


FIG. III.22 c

R_{nPrCl}^{TCE} vs. R_{nPrCl}^{cDCE}

Cl_2 PRESSURE = VARIABLE
 P^H PRESSURE = 21.4 mm
 tDCE PRESSURE = 21.4 mm
 TEMP. = 132.5°C



CHAPTER IV.
DISCUSSION

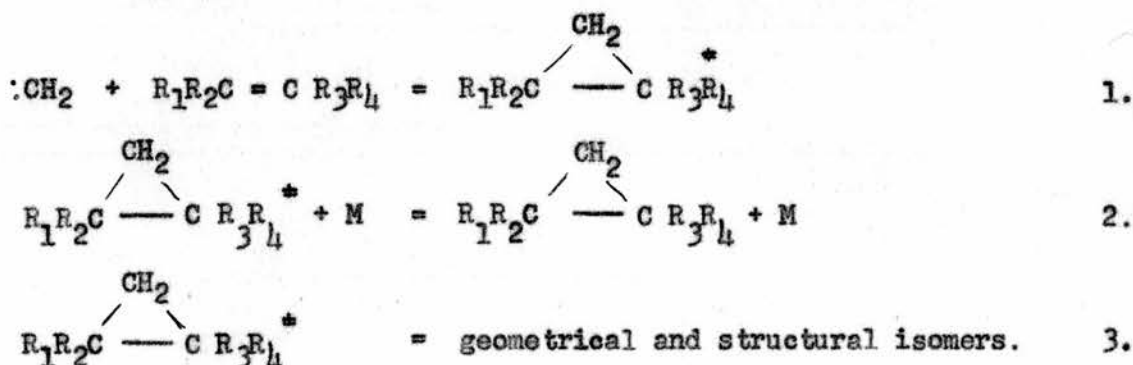
1. Occurrence and Properties of Hot Radicals

It was indicated in the Introduction that the main point of disagreement with regard to the chlorination of olefines is the precise nature of the addition of a chlorine atom to the olefine and in particular the question of whether or not the radical formed should be regarded as an energetic or "hot" entity which can spontaneously decompose thus:



The work presented in this thesis strongly supports the hot radical mechanism: in this respect it is of particular significance that adding a pressure of a chemically inert gas (carbon dioxide) to the reaction mixture has qualitatively the same effect as increasing the pressure of the reactants. The occurrence and properties of hot radicals and molecules will now be considered briefly.

Kistiakowsky and Frey and their collaborators¹⁰⁰⁻¹⁰⁴ have made an extensive study of the addition of methylene to olefines and the proposed mechanism is as follows:



Reaction 1. is about 90 k.cal.mole⁻¹ exothermic and the cyclopropane initially formed will contain this energy together with any excess energy that the methylene

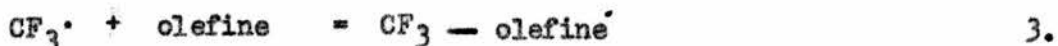
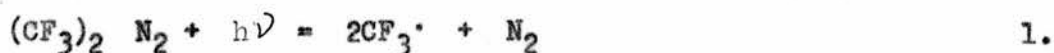
may have. The excess vibrational energy involved is some $30 \text{ k.cal.mole}^{-1}$ greater than that required for the isomerisation of the cyclopropane and isomerisation will occur unless the molecule is stabilised by collision. In agreement with this it was found that the ratio of cyclopropane to isomerisation products formed increased with increasing pressure. Helium, argon, nitrogen and carbon dioxide were all found to be about as effective as the parent molecule in stabilising the hot adduct. By producing the methylene from both ketene and diazomethane and with radiation of different wavelengths, methylene containing different amounts of excess energy was obtained and the subsequent addition reactions thus resulted in different amounts of excess energy in the cyclopropane formed and corresponding changes in the relative amounts of reactions 2. and 3. were observed. As might be expected, the lifetime of the hot molecule was found to increase not only with a decrease in the excess energy but also with an increase in the number of internal degrees of freedom. Thus, using radiation of 3100 \AA , k_3/k_2 was found to be 1.19 atm. in the reaction of ketene with ethylene, 0.06 atm. in the reaction with propylene and 0.0032 atm. in the reaction with isobutene. The corresponding lifetimes were calculated to be $8.4 \times 10^{-10} \text{ sec.}$, $1.7 \times 10^{-9} \text{ sec.}$ and $3.4 \times 10^{-8} \text{ sec.}$, respectively.

In one particularly interesting study Butler and Kistiakowsky¹⁰³ photolysed both ketene and diazomethane with cyclopropane and propylene and using radiation of different wavelengths: the lifetime of the energy rich methyl cyclopropane formed depended markedly on the source of the methylene used and also on the choice between cyclopropane and propylene but the composition of the mixture of butenes produced by isomerisation was the same in all the cases studied and this was interpreted to mean that the excess energy migrates freely

among the normal modes of vibration of the hot methyl cyclopropane molecules between the time of their formation and rearrangement, since the transition state through which the reactions of methylene with cyclopropane and propylene proceed to the same hot intermediate are quite different and, therefore, different modes of vibration in methyl cyclopropane should be initially excited.

There is also a good deal of evidence that the addition of an alkyl radical to a multiple bond gives rise to a vibrationally excited product. Dominguez and Trotman-Dickenson¹⁰⁵ have reported that in the addition of isopropyl and t-butyl radicals to acetylene some pent-1-ene and 4 methyl pent-1-ene, respectively, are formed and they can only arise by migration of a methyl group in the alkenyl radical. This was attributed to the energy available from the addition (about 30 k.cal.mole⁻¹) being sufficient to overcome the barriers to isomerisation unless removed by collision and at high pressures the non-rearranged products, 3,3 dimethyl but-1-ene and 3 methyl but-1-ene accounted for 100% and 95%, respectively, of the total reaction. This again confirms that the lifetime of the energetic radical increases with the number of degrees of freedom. Experiments with added nitrogen showed that it was effective in collisional deactivation, but somewhat less so than the reactants.

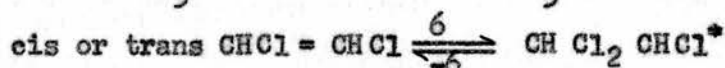
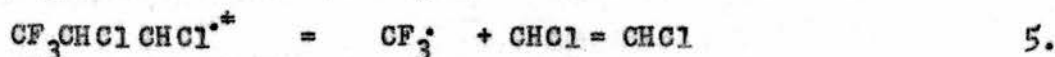
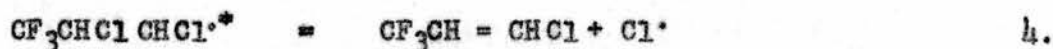
Szwarc and co-workers^{106,107} have investigated the addition of trifluoromethyl radicals to olefines in competition with hydrogen abstraction from 2,3 dimethyl butane which was used as a solvent in the liquid phase and as a diluent in the gas phase. The CF₃· radicals were produced by the photolysis of hexafluoroazomethane:



It was shown that

$$k_3/k_2 = (X_{\text{hydr.}}) / (X_{\text{olefine}}) \left\{ (CF_3H/N_2)_{\text{lost}} / (CF_3H/N_2)_{\text{formed}} \right\}$$

where $X_{\text{hydr.}}$ and X_{olefine} are the mole fractions of the hydrocarbon and olefine respectively, $(CF_3H/N_2)_{\text{formed}}$ represents the ratio of the two in a given experiment and $(CF_3H/N_2)_{\text{lost}}$ represents the difference between $(CF_3H/N_2)_{\text{formed}}$ and the (CF_3H/N_2) ratio found in an experiment with no olefine present. The independence of this function on total pressure at temperatures below 150°C indicated that decomposition of the adduct did not occur. However, it was found that photolysis of 4 mole % $(CF_3)_2 N_2$ in trans dichloroethylene led to complete isomerisation of the olefine at 65°C. This contradictory evidence was reconciled by postulating that the vibrationally excited adduct could decompose by reaction 4 but not by reaction 5 and that the chlorine atom produced was responsible for the isomerisation (reactions 6 and -6).



As evidence for this process, the isomerisation was suppressed in the presence of the saturated hydrocarbon and hydrogen chloride was formed. C—C bond dissociation energies in hydrocarbon radicals¹⁰⁸ are not very different from the value of 20.3 k.cal.mole⁻¹ for D(C₂H₂Cl₂—Cl) and the authors suggested that reaction 5. does not occur because the rupture of a C—R bond where R is polyatomic requires a more detailed energy distribution than the fission of a C—X bond where X is an atom.

Derbyshire and Patrick¹⁰⁹ proposed a similar mechanism for the isomerisation of dichloroethylene induced by CClF₂· radicals. They demonstrated that

isomerisation was the main reaction but were unable to determine whether or not it was in part due to reactions of type 5 but they were able to confirm that $\text{CClF}_2\text{CH} = \text{CHCl}$ was a minor product.

The addition of oxygen atoms, produced by the photolysis of nitrous oxide, to ethylene, propylene, the four butenes, cis-pent-2-ene and tetramethylethylene at room temperature and in the pressure range 50-600 mm was studied by Cveticanovic¹¹⁰ who showed that the adducts had enough vibrational energy to decompose spontaneously. A collisional deactivation effect was noted and the energetic radicals found to have lifetimes of the order of 10^{-8} - 10^{-9} sec. and which increased with increasing complexity of the molecule. On the other hand, Strausz and Gunning¹¹¹ found that the only products of the addition of sulphur atoms to ethylene and propylene were the corresponding sulphides although the addition reaction is ~ 45 k.cal.mole⁻¹ exothermic and they presumed that the energy-rich triplet biradical could reform the cyclic sulphide by collisional deactivation. The difference in behaviour is probably due to the fact that C—O bonds are stronger than C—S and thus a greater amount of energy is made available by the addition of an oxygen atom.

The addition of hydrogen atoms to olefines has been more thoroughly investigated than any other atom addition reaction. A hot radical effect in the addition of atomic hydrogen to ethylene was demonstrated by Bradley, Melville and Robb¹¹² and was strikingly confirmed by Turner and Cveticanovic¹¹³ who investigated the disproportionation/combination reactions of isomeric ethyl radicals formed as follows:



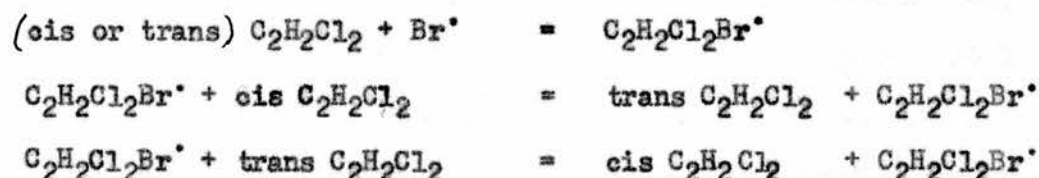
In the latter case the isomeric butenes produced indicated the presence of $\text{C}_2\text{H}_3\text{D}_2^\bullet$ and $\text{C}_2\text{H}_5^\bullet$ as well as $\text{C}_2\text{H}_4\text{D}^\bullet$ whereas in the former the only radical

involved was $C_2H_4D^\bullet$ and this may be understood in view of the difference in the bond dissociation energy between a C—D and a C—H bond arising from a difference in their zero point energies: when an H^\bullet atom adds to CD_4 the radical formed has enough energy to split off an H^\bullet atom but not a D^\bullet whereas the radical formed from $D^\bullet C_2H_4$ has enough energy for either D^\bullet or H^\bullet to be lost and, indeed, both the statistical and energetic conditions favour loss of H^\bullet . A later study of the addition of H^\bullet and D^\bullet atoms to ethylene by Heller and Gordon¹¹⁴ showed that the rate constant for unimolecular decomposition of the energetic radical increased from $14 \times 10^6 \text{ sec}^{-1}$ at $26^\circ C$ to $80 \times 10^6 \text{ sec}^{-1}$ at $203^\circ C$. In a recent series of papers Rabinovitch and his collaborators^{115,116} have outlined their studies on the unimolecular decomposition of hot radicals produced by the addition of H^\bullet or D^\bullet atoms to butenes and D-substituted ethylenes in the temperature range -103 to $+25^\circ C$. The experimental rate constants were compared with those calculated from absolute rate theory and good semi-quantitative agreement was obtained: as predicted by theory the observed rate of decomposition was greater for radicals formed by the addition of D^\bullet and increased with rise in temperature due to an increase in energy of the radicals formed. The predicted variation of the rate constant with pressure was also obtained. Kohlmaier and Rabinovitch¹¹⁷ investigated the efficiency of various molecules in collisional deactivation and deduced that a single collision with the parent olefine removed enough energy to prevent unimolecular decomposition and that the efficiencies of other molecules increased with their molecular weight and complexity but even for helium was of the order of 0.2 of that for the olefine.

The bond dissociation energy D (olefine—I) will certainly be much lower than the corresponding value for chlorine and the addition of an iodine atom should be strongly reversed at quite low temperatures. Noyes et al.¹¹⁸

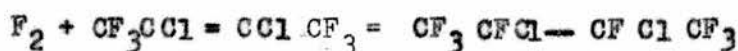
used radioactive iodine to show that iodine atom exchange and cis/trans isomerisation both occur in the reaction between iodine and di-iodoethylene and a similar result was obtained for the bromine/dibromoethylene system by Steinmetz and Noyes¹¹⁹ who calculated that the energy barrier opposing dissociation of a bromine atom from the radical was about 3 k.cal.mole⁻¹.

Ketelaar et al.⁹⁹ pointed out that D(C₂H₂Cl₂-Br) is likely to be about 13 k.cal.mole⁻¹ and suggested the alternative mechanism for the bromine catalysed isomerisation of dichloroethylene:



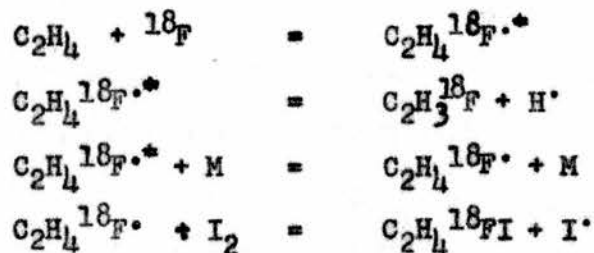
This work was in fact carried out in the liquid phase but it would seem probable that, at least in the gas phase, the ready reversibility of bromine and iodine addition reactions should be partly due to a hot radical effect.

Rodgers¹²⁰ studied the reaction



in the temperature range -20°C to +15°C and found the kinetics to be similar to those for the chlorination of olefines. However, two major products were obtained: CF₃CClF - CClFCF₃ and a product which mass spectral analysis showed only one chlorine atom in the ratio 6:1. This would suggest that the radical formed by the addition of a fluorine atom must be a hot radical since thermal dissociation of a C-Cl bond would be unlikely at such low temperatures. There was no change in the cis/trans ratio of the unreacted olefine, however, indicating that fluorine atoms are not lost from the radical but this is not surprising since C-F bonds are considerably stronger than C-Cl. Colebourne and Wolfgang¹²¹ allowed ¹⁸F atoms to react with ethylene in the presence of

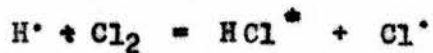
iodine and showed that the $C_2H_4^{18}FI/C_2H_3^{18}F$ ratio decreased from 4.5 to 1 on reducing the pressure from 75 to 5 cm and suggested the mechanism:



It is of interest to note that vibrationally excited products also occur in reactions of the type



¹²² and Polanyi has successfully demonstrated the occurrence of vibrationally excited HCl by studying the infra red chemiluminescence from the reaction



2. The Mechanism of Olefins Chlorination

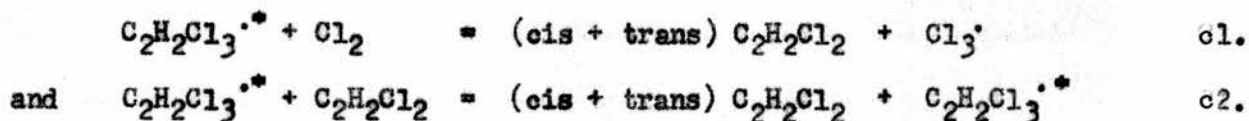
Two main facts emerge from the above review:

- 1) the addition of a radical or atom to a multiple bond produces a vibrationally excited entity which may decompose spontaneously unless deactivated by collision;
- 2) the efficiency of a molecule in collisional deactivation increases with molecular weight and complexity but even the lighter monatomic rare gases are quite effective.

In this context the work described in this thesis together with that of Ayscough, Cocker and Dainton⁴⁶ and the complementary evidence from the addition of halogenomethyl radicals to dichloroethylene^{106,109} proves convincingly that the chlorination of dichloroethylene proceeds via a hot radical mechanism. It would be dangerous to generalise this conclusion to include the other chloroethylenes and ethylene but there is no apparent reason why dichloroethylene should be unique and, indeed, Hagopian^{51,52} and Dainton et al.^{75,79} have provided evidence that a similar mechanism does apply to the chlorination of ethylene, vinyl chloride and trichloroethylene and the conclusion of Goldfinger and co-workers that hot radicals do not participate in the chlorination of ethylene¹²³ and trichloroethylene^{45,123} must be regarded with suspicion. Those workers also found no evidence for hot radicals in the chlorination of tetrachloroethylene and suggested that with increasing chlorine content the energy would be more evenly distributed between low frequency vibrations with a correspondingly greater probability of deactivation compared to decomposition. This, of course, implies that the strongest effect should appear in the case of ethylene and the expected trend was in fact observed by Ayscough, Cocker, Dainton and Hirst⁷⁹ for $C_2H_nCl_{4-n}$, $n = 1-4$.

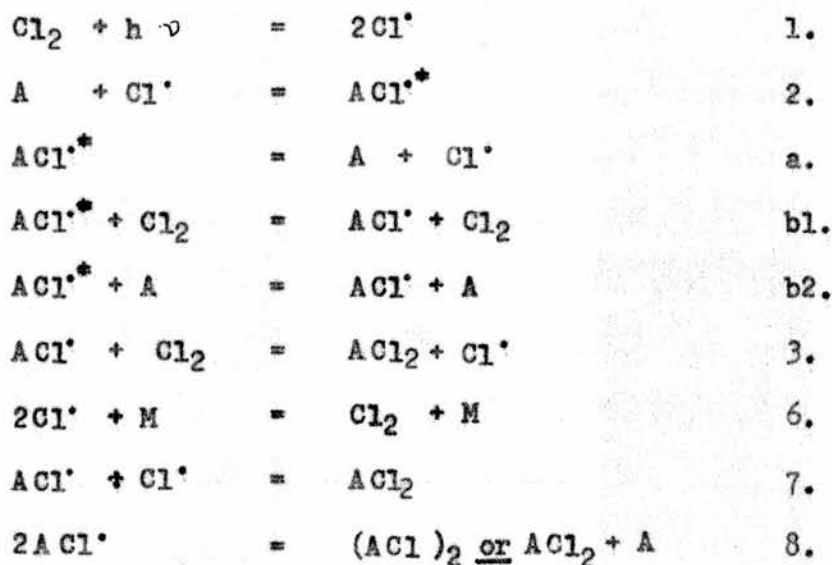
The mechanism proposed by Ayscough, Cocker and Dainton⁴⁶ does, however,

differ in certain respects from that proposed here: they claimed that the olefine was not effective in collisional deactivation whereas our results show that chlorine, the olefine, propane and carbon dioxide all deactivate the hot radical; this is more in line with the expected behaviour. The earlier experiments were carried out over a more restricted range of olefine pressures (30-80 mm Hg.) and it can be seen from table III.4 that the variation of R_{TCE}^{1DCE} over this range is of the same order as the $\pm 10\%$ accuracy claimed. Furthermore, the present work suggests that atom exchange reactions of the type:



do not occur. This conclusion is based on the fact that the graphs of $1/P_{Cl_2}$ against R_{TCE}^{1DCE} are not linear as required by the mechanism of Ayscough, Cocker and Dainton, but are in fact curved and pass through the origin. A similar deduction is made from the corresponding graphs of R_{TCE}^{1DCE} against the reciprocal of olefine pressure (see page 80 and figs. coded a). It follows that equations III.3 - III.5 cannot be used to determine x and the rate constants for deactivation and unimolecular decomposition. Again, the range of $(1/P_{Cl_2})$ studied by the earlier workers ($0.5 - 2.0 \times 10^2 \text{ mm Hg}^{-1}$) was smaller than that investigated in the present experiments and their procedure of carrying out a large number of experiments at three selected pressures less likely to reveal non linearity than that adopted here. It may be noted that no evidence was presented for exchange reactions of this type in any of the hot radical systems discussed above.

The question arises: can the postulated mechanism explain the well established kinetics of olefine chlorination? Including the usual chain terminating steps, the mechanism is (A = olefine) :



and, applying the steady state approximation,

$$R = \frac{(2I_a)^{\frac{1}{2}} k_3 [\text{Cl}_2]}{(k_6 M d^2 + k_7 d + k_8)^{\frac{1}{2}}} \quad \text{IV.1.}$$

which is similar in form to the equation (I.12) derived on the basis of the simple mechanism. In this case, however,

$$d = \frac{k_3 [\text{Cl}_2] (k_a + k_{b1} [\text{Cl}_2] + k_{b2} [\text{A}])}{k_2 [\text{A}] (k_{b1} [\text{Cl}_2] + k_{b2} [\text{A}])}$$

and as 8. is replaced by 7 and then by 6. as the chain ending step the rate law becomes successively -

$$R = \frac{(2I_a)^{\frac{1}{2}}}{(k_8)} k_3 [\text{Cl}_2] \quad \text{IV.2.}$$

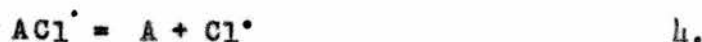
$$R = \left\{ \frac{I_a k_2 k_3 [\text{A}] [\text{Cl}_2] (k_{b1} [\text{Cl}_2] + k_{b2} [\text{A}])}{k_7 (k_a + k_{b1} [\text{Cl}_2] + k_{b2} [\text{A}])} \right\}^{\frac{1}{2}} \quad \text{IV.3}$$

$$R = \frac{(2I_a)^{\frac{1}{2}}}{(k_6 M)} \frac{k_2 [\text{A}] (k_{b1} [\text{Cl}_2] + k_{b2} [\text{A}])}{(k_a + k_{b1} [\text{Cl}_2] + k_{b2} [\text{A}])} \quad \text{IV.4}$$

It was seen in the Introduction that rate laws of the form IV.2 are obtained at high olefine pressures where all the chlorine atoms are used up in reaction 2, and chain ending is entirely by 8. As the olefine pressure decreases and 7, and 6, become more important fractional orders are obtained as given by equations IV.3 and IV.4. The first order dependence on [A] and zero order dependence on [Cl₂] sometimes observed at high chlorine and low olefine pressures become possible when $k_{b1}[Cl_2] \gg (k_a + k_{b2}[A])$ and IV.4 reduces to

$$R = \left(\frac{2I_a}{k_6 M} \right)^{\frac{1}{2}} k_2 [A] \quad \text{IV.5}$$

At high temperatures when reaction 4.



becomes important

$$\alpha = \frac{(k_4 + k_3 [Cl_2]) (k_a + k_{b1}[Cl_2] + k_{b2}[A])}{k_2 [A] (k_{b1}[Cl_2] + k_{b2}[A])}$$

and, if chain ending is by reaction 7.

$$R = \frac{(2I_a)^{\frac{1}{2}} k_3 [Cl_2] \left\{ k_2 [A] (k_{b1}[Cl_2] + k_{b2}[A]) \right\}^{\frac{1}{2}}}{\left\{ k_7 (k_4 + k_3 [Cl_2]) (k_a + k_{b1}[Cl_2] + k_{b2}[A]) \right\}^{\frac{1}{2}}} \quad \text{IV.6}$$

The activation energy for reaction 4 is much greater than that for all the other reactions involved and this mechanism can thus account for the observed maximum in the rate of photochlorination with increasing temperature⁴⁵, and the deduction that $E_4 \sim 20 \text{ k.cal.mole}^{-1}$ and therefore refers to a thermally equilibrated radical does not invalidate the hot radical mechanism.

It can thus be seen that the range of kinetic behaviour exhibited in olefine chlorinations can be interpreted on the basis of the suggested mechanism.

It is difficult to make a direct quantitative comparison of the results

obtained by Ayscough, Cocker and Dainton and those presented in this thesis, but for cis dichloroethylene the range of values of R_{TCE}^{tDCE} obtained by Ayscough et al. at 30°C (0.29-0.54) is of the same order of magnitude as that found in this work at 35°C (0.2-0.37) if the same range of total pressures (90-200 mm Hg) is considered. Unfortunately, the corresponding values for trans dichloroethylene are, respectively, (0.20-0.28) and (0.6-1.5) and there is no obvious way of reconciling the two sets of results. Ayscough, Cocker and Dainton's data lead to the conclusion that the hot trichloroethyl radical decomposes thus:

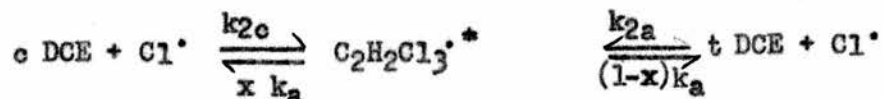


in contrast with our conclusion that:



It is of interest to note at this point that, in the experiments with dibromoethylene, cis and trans chlorobromoethylene were formed in the ration 1.6:1 and cis and trans dichloroethylene in the ratio 2.6:1. The radical from which the dichloroethylenes are formed is in this case $C_2H_2Cl_2Br^*$ but the similarity between the two systems is noteworthy.

If the radicals formed by the addition of a chlorine atom to cis and trans dichloroethylene are the same then



and the equilibrium constant, K_{eq} , is given by

$$K_{eq} = \frac{[t \text{ DCE}]_{eq}}{[c \text{ DCE}]_{eq}} = \frac{(1-x)}{(x)} \frac{k_{2c}}{k_{2t}} \quad \text{IV.7}$$

This expression is independent of k_a and even if the two radicals do differ in

energy the equilibrium constant should still be given by IV.7, provided x is the same in both cases. Using the values calculated in Chapter III

$$K_{eq} = \frac{0.22 \times 8.0}{0.78 \times 3.0} \exp. - \frac{(190+170)}{(RT)}$$

$$K_{eq} = 0.55 \text{ at } 300^{\circ}\text{C.}$$
$$K_{eq} = 0.57 \text{ at } 350^{\circ}\text{C.}$$

Those values may be compared with ones quoted by Pitzer and Hollenberg¹²⁴:

$$K_{eq} = 0.645 \text{ at } 300^{\circ}\text{C.}$$
$$K_{eq} = 0.683 \text{ at } 350^{\circ}\text{C.}$$

The agreement is satisfactory considering the large errors involved in x , k_{2c} and k_{2t} and the values of those functions derived in this thesis can be regarded as reasonable as well as internally consistent.

It has already been shown that k_a , the rate constant for the decomposition of the hot radical increases with temperature and the apparent activation energy is about 1300 k.cal.mole⁻¹. Since the radical already has enough energy to decompose spontaneously the term "activation energy" is somewhat misleading. In fact, the increase in k_a with temperature can be explained in terms of Kassel's theory of unimolecular reactions: if an activated molecule has energy E and the minimum energy for decomposition is E_0 then the rate constant for decomposition is given by

$$k = A \left(\frac{E-E_0}{E} \right)^{S-1} \quad \text{IV.8}$$

where A is the frequency of dissociation of the molecule when E_0 is in the critical oscillator and S is the number of oscillators which contain E and contribute to the dissociation. In this case $E_0 \sim D(\text{C}_2\text{H}_2\text{Cl}_2-\text{Cl})$ and this

energy is available from the exothermicity of the reaction, but the radical also contains excess thermal energy of vibration which increases with increasing temperature (note that part of this excess energy derives from the translational energy of the chlorine atom which must initially be converted into vibrational energy of the complex) and it follows that k_a must increase with temperature. This trend was previously noted by Ayscough, Cocker and Dainton¹¹⁵ for the addition of a chlorine atom to the dichloroethylenes and, as indicated earlier, Rabinovitch and his collaborators^{115,116} have had considerable success in calculating theoretically the rate constants for the decomposition of energetic alkyl radicals formed by hydrogen atom addition to olefines.

The lifetime of the $C_2H_2Cl_3^{\cdot*}$ radicals decreases from 5×10^{-10} sec. at $35^\circ C$ to 3×10^{-10} sec. at $132.5^\circ C$ (table III.23) and this may be compared with values of 2×10^{-8} sec. for $C_2H_2D_3^{\cdot*}$ radicals¹¹⁶ and 9×10^{-8} for $s-C_4H_9^{\cdot*}$ radicals. In the former case the E_0 required to break a C-H bond is of the order of twice that to break a C-Cl bond¹²⁵ and in the latter, although the radicals were formed by adding H atoms to cis butene and the energy available in excess of that required to break a C-C bond ($E-E_0$) therefore large, S_{11} is also large. Considering the way in which those factors operate in equation IV.8 the lifetime given for the $C_2H_2Cl_3^{\cdot*}$ radicals is not unreasonable.

3. Arrhenius Parameters for Chlorine Atom Addition

The Arrhenius parameters for the reaction



in the series $A = C_2H_nCl_{4-n}$, $n = 0-4$ are given in the following table: the value of k_2 calculated at $350^\circ C$ have also been included.

<u>Reaction</u>	<u>log A</u>	<u>E(k.cal.mole⁻¹)</u>	<u>log k₂</u>	<u>Ref.</u>
$C_2H_4 + Cl\cdot$	10.6 ± 0.3	0.58 ± 0.54	10.2	51
	10.2 ± 0.1	0	10.2	52
$C_2H_3Cl + Cl\cdot$	10.3 ± 0.6	1.5 ± 1.0	9.4	79
<i>cis</i> $C_2H_2Cl_2 + Cl\cdot$	10.3 ± 0.4	1.2 ± 0.7	9.6	63
	10.9 ± 0.2	0.19 ± 0.25	10.8	This work
<i>trans</i> $C_2H_2Cl_2 + Cl\cdot$	10.5 ± 0.2	-0.17 ± 0.23	10.6	This work
$C_2HCl_3 + Cl\cdot$	10.3 ± 0.6	1.5 ± 1.0	9.4	79
	9.75	0	9.75	45
$C_2Cl_4 + Cl\cdot$	9.2	0	9.2	50

It is difficult to draw any conclusion about the general trend of those results since the disagreement between different workers for a given reaction is almost as large as the spread of the results for all the reactions. Thus, although the rate constants obtained by Ayscough et al.⁷⁹ and Huybrechts et al.⁴⁵ for the addition of a chlorine atom to trichloroethylene are in good agreement, the corresponding A factors and activation energies are rather different and, in fact, the rate constants were deduced on the assumption of different mechanisms. The A factor obtained in the present work for the addition of a chlorine atom to *cis* dichloroethylene is 0.6 log units higher than that obtained by Ayscough and

co-workers⁶³, the corresponding activation energies are just outside the combined error limits and the rate constants differ by an order of magnitude.

The following general observations may be noted:

1) In the competitive chlorination of propane and ethylene, Hagopian obtained the rate constant ratio $k_2/k_2' (n_{PrH})$ at a total pressure of between 200 and 700 mm Hg at which pressure it was assumed that decomposition of the hot radical was unimportant. From the expected value of k_a (say $10^9-10^{10} \text{ sec}^{-1}$) this conclusion does not seem justified and the A factor quoted is probably best regarded as a minimum value. In addition, since k_a increases with temperature the apparent activation energy difference E_2-E_2' would be too negative and the derived value of E_2 a minimum value. In fact, the Arrhenius plot obtained was badly curved at higher temperatures and this may have been partly due to the increasing importance of radical decomposition. The value given by Martens was reported as a footnote to a paper by Hagopian, Knox and Thomson⁵² and so far as the present author is aware the details have not yet been published.

2) The activation energies reported by Ayscough and co-workers^{63,79} are appreciably higher than the other values that have been obtained for ethylene and the chloroethylenes. The values for vinyl chloride and trichloroethylene were obtained from competitive chlorinations with cis dichloroethylene and thus depend on the results for cis dichloroethylene which were derived from rather difficult rotating sector experiments at very high chlorine pressures, when the chain ending reactions were considered to involve only chlorine atoms. Goldfinger¹²³ has pointed out that for chain ending to be predominantly



the inequality $k_6M \geq k_7$ must hold. Under the conditions used by Ayscough,

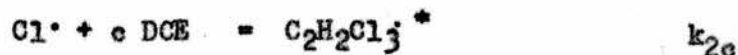
Cocker, Dainton and Hirst and using the values of k_6 , k_3 and k_2 given by them and assuming either their mechanism or the one adopted in this thesis it follows that $k_7 \leq 10^{12}$ l.moles⁻¹ sec.⁻¹ and this may be compared with a value measured by Huybrechts, Meyers and Verbeke⁴⁵ of 8×10^{10} l.mole⁻¹ sec.⁻¹ for the reaction



However, Ayscough et al.'s value for the termolecular rate constant, k_6 , (6.5×10^{11} and 7.2×10^{11} l.² mole⁻² sec.⁻¹ at 39.5°C and 62.1°C, respectively) is somewhat higher than that obtained by other workers:

(6×10^8 l.² mole⁻² sec.⁻¹¹²⁶, 2.9×10^{10} l.² mole⁻² sec.⁻¹¹²⁷, and 2×10^{10} l.² mole⁻² sec.⁻¹¹²⁸) and the possibility of some termination involving $C_2H_2Cl_3\cdot$ radicals cannot be definitely ruled out.

Ayscough and co-workers measured the average lifetime of chlorine atoms (τ) with a mixture of 2 mm cis dichloroethylene and 400 mm chlorine and evaluated the rate constant for the addition reaction



from the equation

$$k_{2c} = R_p \frac{(1 + k_{\beta}/k_{\gamma})}{2I_a \tau [c \text{ DCE}]} \quad \text{IV.9}$$

The term in brackets contributes about 350 cal.mole⁻¹ to the overall activation energy.

If we adopt the mechanism proposed in this thesis, equation IV.9 is replaced by

$$k_{2c} = \frac{R_p}{2I_a \tau [c \text{ DCE}]} \left\{ \frac{k_{ac} + k_{b1} [Cl_2] + k_{b2} [c \text{ DCE}]}{k_{b1} [Cl_2] + k_{b2} [c \text{ DCE}]} \right\} \quad \text{IV.10}$$

Using our values of k_{ac} and k_b the term in brackets has an apparent activation energy of $550 \text{ cal.mole}^{-1}$ so that there is a difference of $200 \text{ cal.mole}^{-1}$ between the values derived on the basis of the different mechanisms and our mechanism gives a value of $E_{2c} = 1 \text{ k.cal.mole}^{-1}$. Since the rate constants for vinyl chloride and trichloroethylene were indistinguishable all three can probably be assigned the value $E_2 = 1.1 \text{ k.cal.mole}^{-1}$.

As pointed out above, the value of k_2 for cis dichloroethylene obtained by Ayscough, Cocker, Dainton and Hirst is an order of magnitude lower than that obtained from the present work. Since the error in k_2/k_1 , obtained from our competitive experiments is about $\pm 10\%$ this implies either that the assumed rate constant for the abstraction of a hydrogen atom from propane is too high or that the value of k_2 obtained by Ayscough et al. by using the rotating sector technique is too low. The latter possibility seems more likely due to the difficulty of the experiments, the requirement of extreme purity of the reactants and the assumptions that have to be made about the chain ending reactions.

3) It has already been noted that, due to the possible occurrence of some surface reaction at high chlorine pressures, the values of A_2 and E_2 derived from this work for cis dichloroethylene should be regarded as maximum and minimum values respectively. The apparently negative value of E_2 for trans dichloroethylene may indicate that there was some interference from surface reaction in this case too, but the results obtained by varying the pressure of the various components of the reaction mixture agreed rather well and interference from surface reaction seems unlikely. Negative activation energies have been obtained for termolecular reactions¹²⁹ but are not usually found for bimolecular processes and the following possibilities arise:

- a) an overall error in E_2 ; ($n \text{ PrH}$) assuming the standard value for hydrogen to be correct;

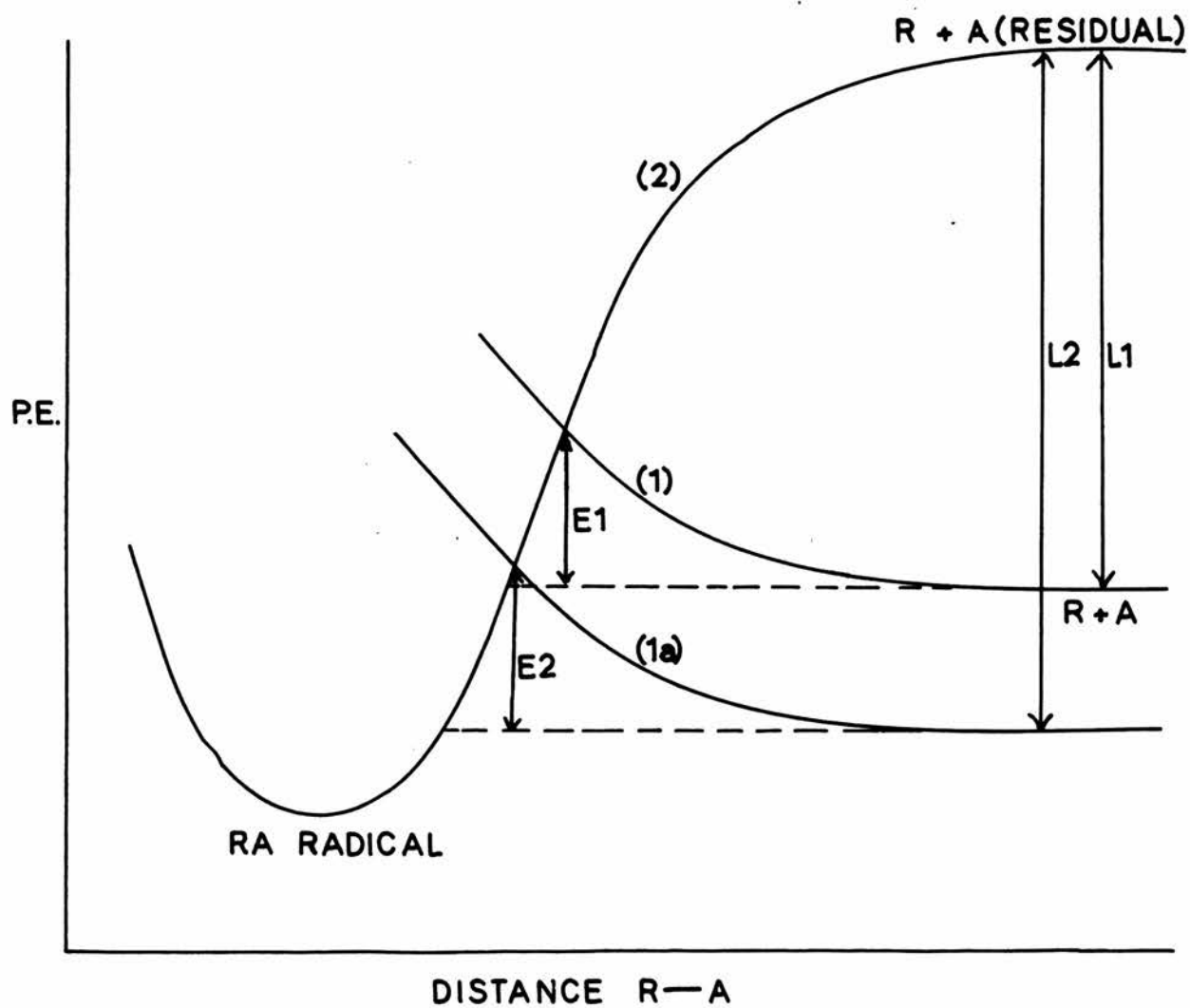
b) an overall error in E_2' (n PrH) assuming the standard value for hydrogen to be in error.

Both a) and b) may make contributions: E_2' (n PrH) was determined as the result of three successive competitive reactions and it would not be surprising if there were small errors in each, although it must be emphasised that the internal consistency of the results was excellent³⁴; the values for hydrogen were obtained by combining the results of three separate sets of experiments carried out at widely different temperatures and the Arrhenius plot obtained was good. However, the activation energy derived from the individual sets of results^{10,41} was some 500-600 cal.mole⁻¹ higher than that obtained by combining them and it is possible that the chosen standard value is a few hundred cal. per mole too low.

4) In an interesting series of papers Szwarc and co-workers^{107,130} have shown that there is a linear relationship between the logarithm of the localisation energy and the logarithm of the rate constant for the addition of a radical to a series of compounds with the same reactive centre and this is explained in terms of the energy diagram in fig.IV.1. Curve (1) represents the repulsion between the radical and the molecule and curve (2) represents the attraction between the radical and "residual A" in which an electron is localised at the reactive centre. L_1 is equal to either the localisation energy or the singlet-triplet excitation energy and the crossing point of the two curves represents the transition state, the difference in energy between this point and the $R^{\cdot} + A$ level being equal to the activation energy, E . For reaction between the same radical and a series of different molecules with the same reactive centre it is assumed that the shape of the repulsion curve remains the same, although the magnitude of the singlet-triplet state energy changes — curve (1a). It is easily seen that as L increases E increases.

It appears that the triplet state is the same for cis and for trans dichloroethylene¹³¹ and, since the singlet state of cis dichloroethylene is more stable than that of the trans isomer, the singlet-triplet excitation energy and hence the activation energy for addition reactions must be greater for cis dichloroethylene than for trans dichloroethylene in agreement with the results given above.

FIG. IV.1



CHAPTER V.

C O N C L U S I O N

It is obvious that our knowledge of the mechanism of the chlorination of ethylene and the chloroethylenes and of the Arrhenius parameters for the addition of a chlorine atom to the double bond remains unsatisfactory. The Arrhenius parameters that are available have been obtained by making different assumptions about the reaction mechanism and the experimental techniques that have been used have proved largely inadequate to measure with certainty the rather small differences between the members of the series. It is considered, however, that the experimental technique of the present work has allowed the mechanism of the chlorination of cis dichloroethylene and of trans dichloroethylene to be firmly established and the rate constants for the chlorine atom addition reactions to be measured with greater precision and less ambiguity than has hitherto been possible. As discussed earlier in this thesis, rate constants measured in competitive experiments are likely to be more reliable than those measured directly and, if the A factor for the addition of a chlorine atom to cis dichloroethylene obtained in the present work is accepted, the competitive experiments of Ayscough et al.⁷⁹ give the same value of $\log A = 10.9$ for vinyl chloride and trichloroethylene. The A factors for trans dichloroethylene and ethylene are probably somewhat lower and the only value available for tetrachloroethylene very much lower. In all cases the activation energies are low and probably less than $1 \text{ k.cal.mole}^{-1}$. It may be noted that Johnston and Goldfinger¹³² have predicted an activation energy $\sim 1 \text{ k.cal.mole}^{-1}$ for all of those reactions on the basis of activated complex theory and by alternatively assuming that they proceeded with zero activation energy the following values of $\log k_2$ were calculated:

	C_2H_4	C_2H_3Cl	C_2HCl_3	C_2Cl_4
Log k_2	11.3	11.3	11.2	11.3

The authors suggest, however, that the activated complex theory in its present form is only of predictive value for bimolecular gas phase reactions if the activation energy is not too low.

Application of the technique of the present work to the other chloroethylenes should provide good evidence as to whether or not the hot radical mechanism operates, but unfortunately would not allow the relevant rate constants to be measured since, in contrast with the dichloroethylenes, the radical decomposition reaction could not be followed experimentally in those cases. In principle it should be possible to achieve this by measuring the rate of incorporation of radioactive chlorine (^{38}Cl) into the olefine but the half life of the isotope (37.5 mins) is much too short to make its use in kinetic studies a practical proposition, although it may prove possible to use it to answer qualitatively the question of whether or not the radicals do decompose. Alternatively, computer analysis of the experimental data from competitive experiments with non-radioactive chlorine may allow the rate constants to be derived.

It would obviously be of interest to study other systems in which direct evidence for hot radical formation could be obtained by following the radical decomposition: the cis and trans isomers of difluoroethylene and dichlorodifluoroethylene may prove of value in this respect.

A P P E N D I X

Column Oven and Temperature Programmer

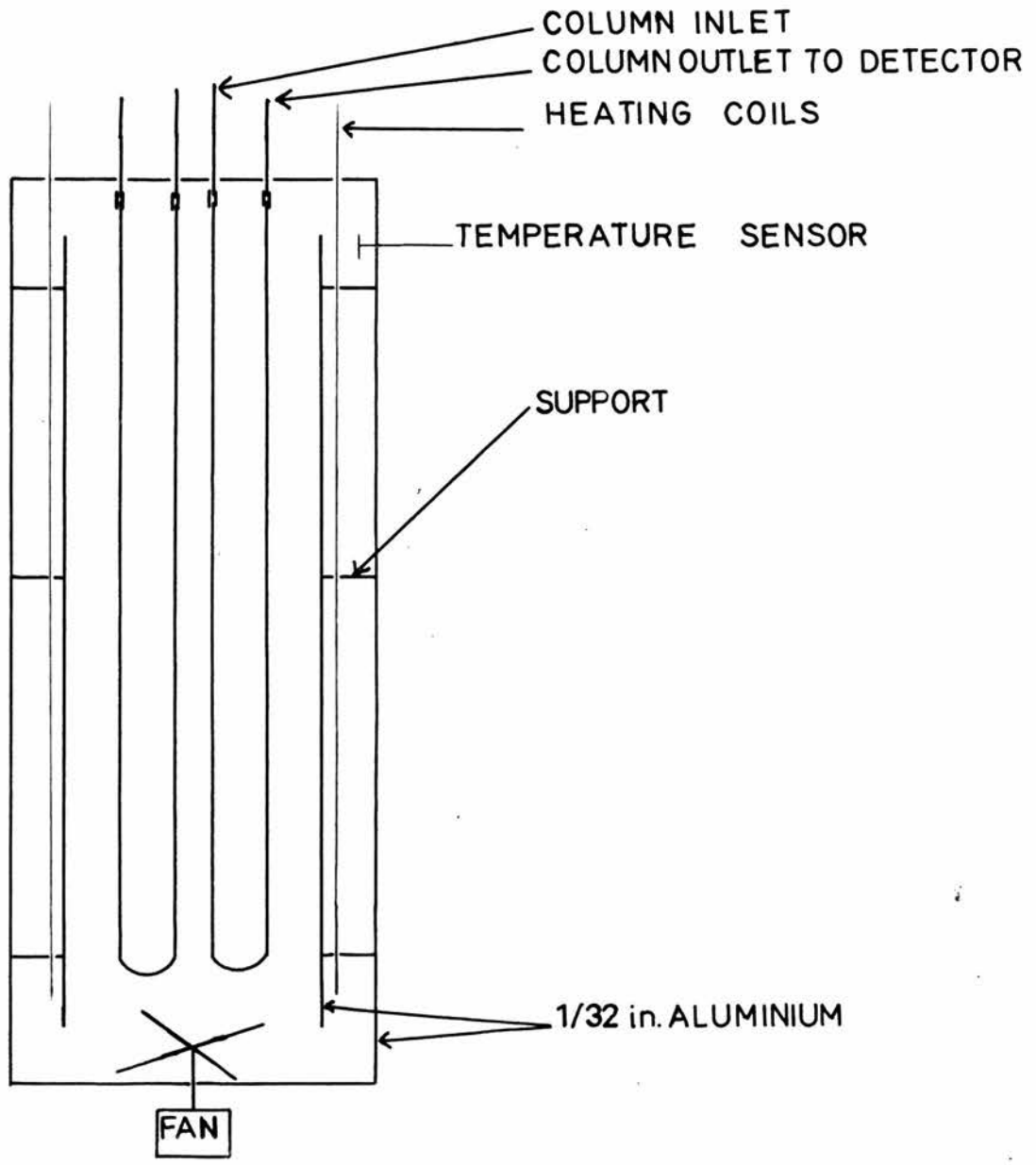
The column oven is shown diagrammatically in the figure overleaf and the circuit diagram for the temperature programmer in an insert on the back cover.

The oven was of low heat capacity and was constructed from 1/32 in. aluminium sheet. The heating coils were wound on the interior wall and a uniform temperature was maintained throughout the oven by a forced circulation of air. The filament of a 40 watt 250 volt bulb, which had a linear resistance/temperature characteristic and a fast response, was used as the sensory element and was incorporated in a bridge circuit. The temperature controller was a D.C. amplifier which sensed out-of-balance signals from the bridge circuit and operated relays T1 and L_o to control the heating circuit.

The Timer operated relay P at predetermined intervals in the range of 1 pulse every 5 secs. to 1 pulse every 55 secs. The uniselector US1 provided an increment in resistance equivalent to a change of 1C^o for each step and its drive magnet was controlled by contacts P1 and PB1 so that US1 was stepped each time relay P released after a timing pulse. After 25 steps relay A was operated via US3 and on the 26th step the MS1 magnet was pulsed via A1 and B1. This switched in a 13.8 ohm resistor to simulate 25 (.055 ohm) steps and US1 then resteped using the same resistors to provide an increment. Each point of US1 was, therefore, equivalent to a 1C^o increment and each MS1 step to a 25C^o increment and provision was made for a temperature range of up to 200C^o.

Switches SW1 and SW2 were used to switch relay S to the appropriate contact on the US5/6-MS2 selector banks so that when the wipers reached this setting relay S was operated to reset the timer and hold the oven at the same temperature until further programmed. The selectors could also be stepped by

COLUMN OVEN



a manual pulse button and this could be used to set the controller to a predetermined temperature or to zero it after use.

The facilities available allowed the column oven to be thermostatted at 5°C intervals in the range ambient - 200°C and provided for programming at a rate of $1^{\circ}\text{C}/\text{min}$ to $12^{\circ}\text{C}/\text{min}$ in this range. Under the conditions used the programme was linear and reproducible to $\pm 2^{\circ}\text{C}$.

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