

THE EFFECT OF PYRIDINE AND SOME  
AMINE SALTS ON AROMATIC CHLORINATION

I. RATES AND MECHANISM

II. FORMATION OF TRICHLORIDE ION

by

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A Thesis

Submitted to

the Faculty of Graduate Studies

Research of the University of Manitoba

in Partial Fulfillment of the Requirements

for the Degree of Master of Science

October 1966

## ACKNOWLEDGMENTS

I would like to express my appreciation to Dr. G. E. Dunn who first aroused my interest in physical organic chemistry by his lecture courses in reaction mechanisms. He suggested this research topic and offered helpful suggestions and criticism throughout the course of the work.

A special thanks to Barry Blackburn whose three years research on the related topic of bromination were an invaluable help. Much of the work in this thesis is a result of preliminary work by him. Also a great many of the preparations and purifications of chemicals are the result of the combined efforts of both of us.

I also wish to thank the National Research Council for financial aid in the form of a bursary.

## ABSTRACT

### I RATES AND MECHANISM

The rates of reaction have been measured for the chlorination of p-chloroanisole in chloroform both in the pure solvent and in the presence of added electrolytes: pyridine, pyridine hydrochloride, HCl, N-ethylpiperidine hydrochloride, tetrabutylammonium chloride, and tetrabutylammonium perchlorate. The results are consistent with a rate expression of the form

$$-\frac{d(\text{Cl}_2)}{dt} = k(\text{ArH})(\text{Cl}_2)(\text{Electrolyte})$$

although the first order in electrolyte term is not obeyed for pyridine and tetrabutylammonium chloride. Rate data have also been obtained for the chlorination of toluene in acetic acid both in the pure solvent and in the presence of pyridine, pyridinium nitrate and lithium chloride. The reactions obey the rate expression

$$-\frac{d(\text{Cl}_2)}{dt} = k(\text{ArH})(\text{Cl}_2)$$

The kinetic data indicate that pyridine and pyridine hydrochloride are not especially effective as catalysts for aromatic chlorination. The results are best interpreted by assuming that the increase in rate is due to an increase in polarity of the solvent medium.

## II TRICHLORIDE ION

The trichloride ion formation constant has been measured for the system tetrabutylammonium chloride - chlorine in chloroform by a spectrophotometric method. The value obtained is  $K = 17 \pm 3 \text{ lt. mole}^{-1}$ .

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## INTRODUCTION

### I KINETICS

Since the claim by Cohen (16) in 1908 that pyridine could function as a catalyst in aromatic halogenation, numerous authors (60, 67) have mentioned its use and in some cases (17, 23, 25, 32, 52) used it as a catalyst. All of these studies were synthetic organic chemistry and only Yeddanapalli and Gnanapragasam (72) have done any kinetic work in their brief study of the bromination of anisole in carbon tetrachloride with pyridine. In fact very few quantitative studies of catalytic aromatic halogenation have been attempted because the normal catalysts such as metals and metal halides make it difficult to work with a one phase system required for meaningful kinetic data (47). The purpose of this research was, therefore, to study the catalytic effect of pyridine on aromatic chlorination and, perhaps, arrive at some conclusions as to the mechanism of the reaction.

Rate studies were carried out for the chlorination of toluene in acetic acid and p-chloroanisole in chloroform both in the presence of pyridine, pyridine hydro-

chloride, and other added electrolytes as well as in the pure solvent itself. Also a preliminary study was made of Cohen's method (16) for the preparation of chlorobenzene from benzene in the presence of pyridine. The results are discussed in terms of the overall mechanism for aromatic chlorination.

## II TRICHLORIDE ION FORMATION

During the course of the kinetic work it was discovered that tetrabutylammonium chloride had a large effect on the absorbance of chlorine in chloroform. This effect was presumably caused by the formation of another absorbing species in the solution, namely trichloride ion. Since there is some doubt as to the magnitude of the trichloride ion formation constant (45, 59, 73) and, in fact, some doubt as to the existence of trichloride ion (35, 69), a study of this system could lead to some useful conclusions. The trichloride ion formation constant was therefore determined by a modification of the Benesi-Hildebrand (6) spectrophotometric method. A discussion of the experimental value obtained in comparison to other literature values and in terms of the kinetic data is also given.

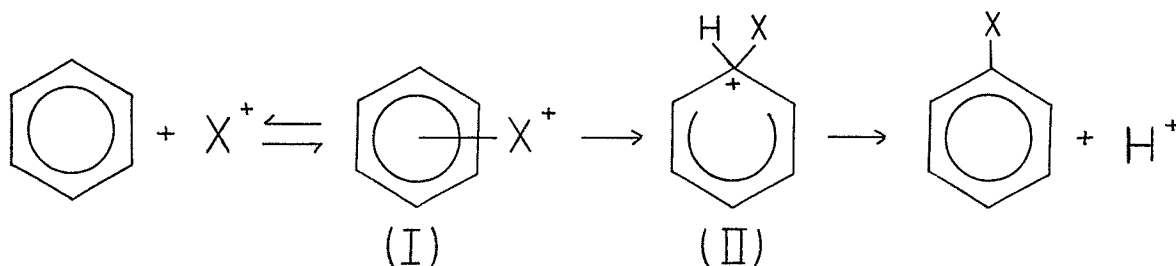
## REVIEW OF THE LITERATURE

## I ELECTROPHILIC AROMATIC CHLORINATION

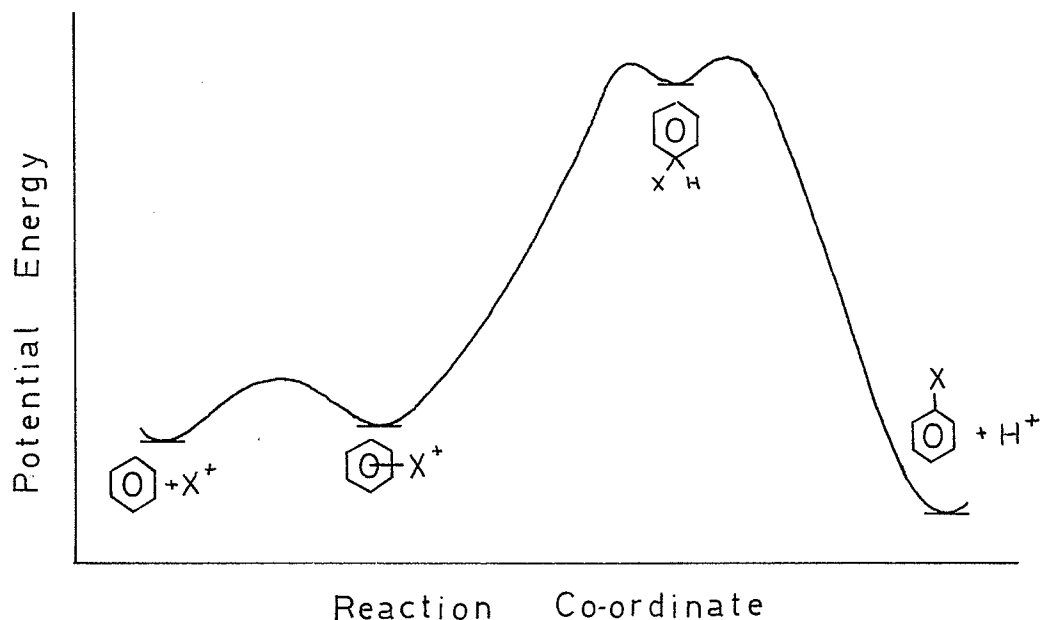
## A NON-CATALYTIC

Since 1911 when Orton and King (49) published their work on the rates of chlorination of anilides in acetic acid, electrophilic aromatic chlorination by molecular chlorine has been extensively studied. These studies have led to well established mechanism for the reaction which can explain the nature and reactivity of the attacking electrophile, the nature of various intermediates and transition states in the mechanism, the kinetic order with respect to aromatic substrate and chlorine, and the quantitative results of the reactivity of various positions in a given aromatic nucleus.

Most aromatic substitutions reactions conform to a simple mechanism (64) involving the rate determining formation of a new bond between the electrophile ( $X^+$ ) and an aromatic carbon atom to form a  $\sigma$ -bonded complex (II). A more general mechanism provides for the reversible formation of a  $\pi$ -complex (I). This mechanism is shown below along with a potential energy diagram.







The experimental results that led to an adoption of this mechanism for electrophilic aromatic chlorination will now be reviewed.

The kinetic order of the reaction is firmly established as second order; first order in chlorine and first order in aromatic substrate according to the rate equation.

$$-\frac{d(\text{Cl}_2)}{dt} = k_2(\text{ArH})(\text{Cl}_2)$$

This has been found true in acetic acid (10, 11, 13, 20, 33, 36, 49), aqueous acetic acid (62), carbon tetrachloride and trifluoroacetic acid (37), as well as ethylene chloride, acetic anhydride, nitromethane and acetonitrile (3). This order with respect to chlorine is of special interest

because aromatic halogenations are often of higher than first order in halogen, especially in non-polar solvents. For instance, the bromination of mesitylene and penta-methylbenzene in chloroform is second order in bromine and first order in aromatic (34) according to the rate equation.

$$-\frac{d(\text{Br}_2)}{dt} = k_3(\text{ArH})(\text{Br}_2)^2$$

and in acetic acid the overall kinetic form for the bromination reaction is of the form (54)

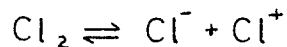
$$-\frac{d(\text{Br}_2)}{dt} = (\text{ArH}) \left[ k_2(\text{Br}_2) + k_3(\text{Br}_2)^2 + k_4(\text{Br}_2)^3 \right]$$

The most reasonable explanation for these higher order bromine terms is that an extra molecule of bromine assists in the breaking of the bromine-bromine bond in the electrophilic reagent by the formation of tribromide ion. This is consistent with the fact that factors which would promote this heterolysis of bromine (e.g. added salts or water in the medium) tend to reduce the overall order (7, 35, 74). In other words some reagent, E, is necessary to polarize the bromine-bromine bond and in the absence of any catalyst or a suitable solvent another bromine molecule can function as this reagent.

Since chlorinations have never been observed with higher than first order in chlorine it seems that a chlorine molecule can not act as the reagent E. This is confirmed by the fact that in non-polar solvents such as

carbon tetrachloride and ethylene chloride the reactions are extremely slow and often subject to induction periods unless an additional catalyst, such as HCl, is added (3,37). In more polar media such as acetic acid or aqueous acetic acid the solvent itself can serve as the reagent E.

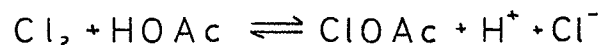
Initially it was concluded that in the chlorination of aromatic compounds no mechanism other than the direct interaction between molecular chlorine and the aromatic substrate came into play (11). However there were some arguments in favor of the extremely reactive  $\text{Cl}^+$  ion or some other positive chlorinating agent being formed in the solution. This is especially true in light of the evidence for positive halogenating agents in solutions of hypochlorous acid in acetic acid. This type of chlorination, which has been reviewed by Ridd and de la Mare (23), will not be discussed here. Robertson has discussed the evidence for molecular chlorine in acetic acid as the effective reagent (55). Added electrolytes show only a small positive catalysis which is in the order of their conductivities;  $\text{HClO}_4 > \text{LiCl} \approx \text{HCl} > \text{NaOAc}$  (20). The slight influence of chloride ion shows that a mechanism involving  $\text{Cl}^+$  ions is not possible. The equilibrium for the reaction



should be greatly affected by added chloride ion and hence

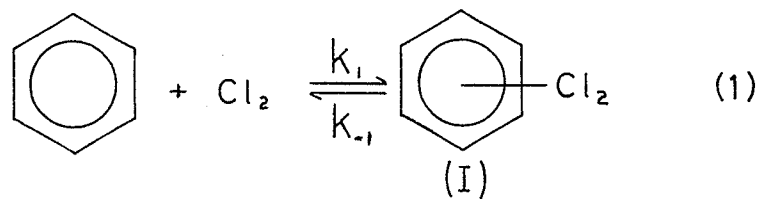
the rate should be decreased if the reaction proceeded by a mechanism involving  $\text{Cl}^+$ . However the rate is in fact slightly increased.

It has also been suggested that in acetic acid chlorine acetate might be the electrophilic reagent



However again since added chloride ion has only a small increase on the rate of reaction this seems unlikely. Also chlorine acetate has been prepared in acetic acid solution and its kinetics investigated (21). The solutions are rapidly decomposed by chloride ion and the chlorinations are enormously catalyzed by mineral acids. This type of chlorination is, therefore, markedly different from a solution of chlorine in acetic acid.

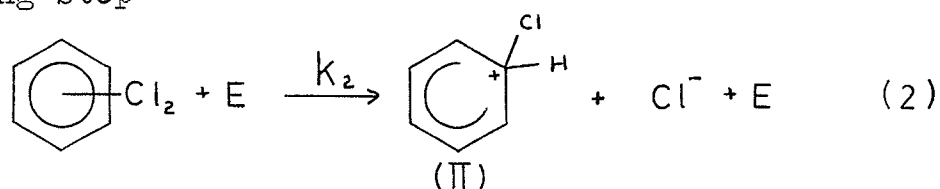
These experimental facts indicate that the attacking electrophilic reagent is the chlorine molecule itself. The first step in the mechanism would therefore be expected to be some interaction between chlorine and the aromatic substrate. The formation of a  $\pi$ -type complex (I) seems quite probable.



Andrews and Keefer (4) have outlined the evidence for

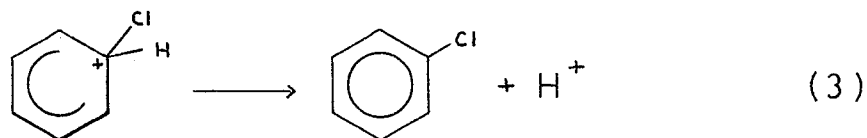
this type of aromatic-halogen complex and discussed the measured values of equilibrium constants for systems similar to reaction 1. In this type of complex the aromatic sextet as a whole acts as the electron donor for the Lewis acid, chlorine.

The second step of the mechanism involves the conversion of this  $\pi$ -complex to a  $\sigma$ -complex (II) in a rate determining step



It is in this step that the reagent, E, is necessary to polarize the chlorine-chlorine bond.

The third and final step is the rapid loss of a proton from the  $\sigma$ -complex to form the product



This step is generally considered to be rapid because there is no evidence for hydrogen isotope effects in aromatic chlorination (5) and in fact very few cases of isotope effects in electrophilic aromatic substitution (75).

The rate of the reaction will be determined by equation 2.

$$\text{Rate} = k_2(\pi\text{-complex})(\text{E})$$

However the concentration of  $\pi$ -complex is controlled by the prior equilibrium in equation 1. Therefore,

$$(\pi\text{-complex}) = \frac{k_1}{K_{-1}}(\text{Cl}_2)(\text{ArH})$$

and

$$\text{Rate} = \frac{-d(\text{Cl}_2)}{dt} = \frac{k_1 k_2}{K_{-1}}(\text{Cl}_2)(\text{ArH})(\text{E})$$

Since the reagent E is often the solvent (as in the case of acetic acid, trifluoroacetic, and acetonitrile) the rate of reaction will appear to be first order in chlorine and first order in aromatic. However in non-polar solvents such as carbon tetrachloride and ethylene chloride the order with respect to E, an added reagent such as HCl, should be observed. This order will be complicated by the fact that the added reagent will have two effects; first, to act as the reagent and second, to increase the polarity of the medium as a whole. This second effect may be quite important because the intermediate  $\sigma$ -complex is a positively charged species and hence the transition state leading to the  $\sigma$ -complex in the rate determining step will likely be more polar than the neutral molecules in the  $\pi$ -complex. This type of reaction is always extremely dependent on the polarity of the medium. Proof of this fact is given by the extremely large catalytic effect of water in acetic acid (10, 54, 62) presumably by changing the polarity of the solvent.

There is other evidence for the rate determining step in non-catalytic chlorination being the formation of the  $\sigma$ -complex. Brown and Brady (12) have shown that the rate of chlorination of methylbenzenes is proportional to their  $\sigma$ -complex basicity rather than their  $\pi$ -complex basicity. This would imply that the transition state in the rate determining step is similar to the  $\sigma$ -complex and hence reaction 2 is rate determining. An excellent discussion of complexes and their role in electrophilic aromatic substitution has been published by Olah (48).

A great deal of the recent work on electrophilic substitution has dealt with the quantitative aspects of rates and isomer ratios. Such quantitative relationships as the selectivity rule and the Hammett equation have been extremely useful in predictions of reaction rates, but have led to no major changes in the overall picture of the mechanism. Stock and Brown (64) have published a lengthy review on this topic and it will not be dealt with further here.

## B CATALYTIC CHLORINATION

In view of the fact that this work is concerned with the effect of a catalyst, pyridine, in aromatic chlorination a short discussion of other catalytic chlorinations will be given. There are, of course, numerous references to the use of catalysts such as iron, ferric chloride,

aluminum chloride, and iodine in the literature (23) but the majority of these were synthetic studies only. Recently, however, a few quantitative studies of rates and products have been used to establish a clearer mechanistic picture.

Jungers and his co-workers have carried out a series of aromatic chlorinations in concentrated media (19, 41, 42, 51, 57). For instance, the chlorination of benzene and alkylbenzenes in excess aromatic as solvent with  $\text{SiCl}_4$  as catalyst has been shown to be first order in aromatic, first order in chlorine, and first order in catalyst (41). The chlorination in a similar system with  $\text{HCl}$  as catalyst is first order in chlorine and first order in  $\text{HCl}$  at low concentrations ( $<0.4$  moles/litre) but of higher order at higher concentrations of  $\text{HCl}$  (57).

Another similar series of studies has been carried out by Lebedev and co-workers (39, 40) using such catalysts as  $\text{AlCl}_3$ ,  $\text{SnCl}_4$ ,  $\text{TiCl}_4$ ,  $\text{FeCl}_3$ ,  $\text{ZrCl}_4$  and  $\text{I}_2$ . They report that the reactions are first order in chlorine, aromatic and catalyst for  $\text{AlCl}_3$ ,  $\text{SnCl}_4$  and  $\text{TiCl}_4$  (40). They also discuss the activity of various catalysts by use of the ratio of rate constants for benzene and toluene,  $\frac{k_T}{k_B}$ . The values given for the ratio of  $\frac{k_T}{k_B}$  for the various catalysts are 3.5 ( $\text{AlCl}_3$ ); 6.4 ( $\text{FeCl}_3$ ); 53 ( $\text{ZrCl}_4$ ); 143 ( $\text{SnCl}_4$ ); and 275 ( $\text{I}_2$ ). Olah (47) contends that the values for  $\text{FeCl}_3$  and  $\text{AlCl}_3$  may be erroneous because of undissolved



catalyst. This type of two phase system makes interpretation of rate data nearly impossible. Olah reports a value of  $\frac{k_T}{k_B}$  of 14.8 for  $\text{FeCl}_3$  in his system.

Some discussion of the significance of the ratio is necessary at this point. For the case where molecular chlorine is the electrophile the ratio of  $\frac{k_T}{k_B}$  is very high. For instance, in acetic acid  $\frac{k_T}{k_B} = 344$  (13) and in nitromethane  $\frac{k_T}{k_B} = 2,440$  (63). The explanation for these values is that molecular chlorine is a weak electrophile and hence the rate of reaction will be greatly affected by the reactivity of the aromatic. In other words the electrophile is quite selective and will react much more readily with an aromatic having a higher electron density. It is this type of selectivity that Brown discusses quantitatively in his review article (64).

The converse of this type of selectivity also applies. Therefore, as Olah (47) discusses, if  $\frac{k_T}{k_B}$  is quite low, as it is for the metal halide catalysts  $\text{AlCl}_3$  and  $\text{FeCl}_3$ , the implication is that the electrophile is no longer very selective. A completely non-selective reagent would have  $\frac{k_T}{k_B} = 1$  and react with benzene and toluene at the same rate. The large decrease in selectivity for these catalysts implies that molecular chlorine is no longer the electrophilic reagent. In fact with the series

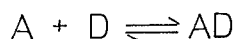
Catalyst	$\text{AlCl}_3$	$\text{FeCl}_3$	$\text{ZrCl}_4$	$\text{SnCl}_4$	$\text{I}_2$
$\frac{k_T}{k_B}$	3.5	6.4	53	143	275

Lebedev (39) feels that the catalyst forms an intermediate complex with chlorine of different degrees of polarization. The formation of  $Cl^+$  may be the limiting case occurring with the most active catalysts. This explanation also accounts for the fact that the reactions are first order in catalyst.

However it should be noticed that this is not the only place in the mechanism for a catalyst to act. As discussed in the section on non-catalytic chlorination, some reagent is necessary to polarize the chlorine-chlorine bond in order to convert the  $\pi$ -complex to the  $\sigma$ -complex in the rate determining step. It appears, therefore, that although the mechanism for catalytic activity seems to be the polarization of the chlorine-chlorine bond, the point in the mechanism at which this polarization occurs is in some doubt.

## II SPECTROPHOTOMETRIC DETERMINATION OF EQUILIBRIUM CONSTANTS

If two species interact in solution to form a Lewis acid base type complex (AD)



and if AD absorbs somewhere in the visible or ultra-violet spectrum it is theoretically feasible to measure the equilibrium constant for the formation of AD by a spectrophotometric method. Benesi and Hildebrand (6) first derived

the relationship necessary for the evaluation of the equilibrium constant and numerous modifications (29, 56, 58), which are the same in principle, are also available. Before proceeding with the derivation the symbols used throughout will be defined.

$C_A^\circ$ ,  $C_D^\circ$  refer to the initial concentration of A and D respectively.

C refers to the equilibrium concentration of the complex AD.

$\epsilon_A, \epsilon_D, \epsilon_c$  refer to the absorptivity of A, D, and AD respectively

$$\epsilon = \epsilon_c - \epsilon_A - \epsilon_D$$

K refers to the equilibrium formation constant of AD in terms of the concentrations of the species A, D, and AD. Note that K is not a thermodynamic constant since no account is taken of activity coefficients.

A refers to the measured absorbance of the solution.

$D = A - \epsilon_A C_A^\circ - \epsilon_D C_D^\circ$  refers to the absorbance of the solution minus the absorbance due to the concentrations  $C_A^\circ$  and  $C_D^\circ$ .

The equilibrium constant for the reaction 4 is defined by

$$K = \frac{C}{(C_A^\circ - C)(C_D^\circ - C)} \quad (5)$$

Experimental conditions are chosen so that  $C_D^\circ \gg C_A^\circ$  and therefore  $C_D^\circ - C \simeq C_D^\circ$ . Therefore

$$K = \frac{C}{(C_A^\circ - C) C_D^\circ} \quad (6)$$

From equation 6

$$C = \frac{KC_0^o C_A^o}{1 - KC_0^o} \quad (7)$$

Now in general the absorbance of the solution will be given by

$$A = \epsilon_c C + \epsilon_A(C_A^o - C) + \epsilon_b(C_b^o - C) \quad (8)$$

assuming all species absorb at the wavelength under consideration. Rearranging equation 8 gives

$$A = \epsilon_A C_A^o + \epsilon_b C_b^o + (\epsilon_c - \epsilon_A - \epsilon_b) C \quad (9)$$

Substituting in the defined values

$$D = A - \epsilon_A C_A^o - \epsilon_b C_b^o \quad \epsilon = \epsilon_c - \epsilon_A - \epsilon_b$$

gives  $D = \epsilon C$  (10)

However C has been defined before in equation 7 in terms of K and the initial concentrations  $C_A^o$  and  $C_b^o$ . Therefore

$$D = \frac{\epsilon K C_A^o C_b^o}{1 - K C_0^o} \quad (11)$$

Rearranging equation 11 gives the initial Benesi-Hildebrand equation

$$\frac{C_A^o}{D} = \frac{1}{K\epsilon} \cdot \frac{1}{C_b^o} + \frac{1}{\epsilon} \quad (12)$$

A slightly different form of this equation was used in this work which can be easily obtained by multiplying equation 12 by  $C_b^o \epsilon$  to give

$$C_b^o = \frac{\epsilon C_0^o C_A^o}{D} - \frac{1}{K} \quad (13)$$

This equation is of the form  $Y = mx + b$  and therefore a

plot of  $C_B^\circ$  versus  $\frac{C_A^\circ C_B^\circ}{D}$  should give a straight line from which the value of  $K$  and  $\epsilon$  can be easily obtained.

An alternate, more general expression, has been derived by Rose and Drago (56) which includes cases where  $C_B^\circ$  is not much greater than  $C_A^\circ$ . Their equation 14 is more complicated and the solution is slightly different.

$$\frac{1}{K} = \frac{D}{\epsilon} - (C_B^\circ + C_A^\circ) + \frac{C_A^\circ C_B^\circ \epsilon}{D} \quad (14)$$

One method is to solve equations simultaneously for two different experimental values of  $D$  for different values of  $C_B^\circ$  and  $C_A^\circ$ . This method will become quite tedious if many experimental determinations are made. A computer technique will greatly simplify this procedure (53) or alternatively the graphical method initially suggested by Rose and Drago can be used.

Although the tendency in recent years has been to readily accept the existence of these electron donor-acceptor complexes, several authors (18, 29, 53) have criticized the experimental evidence provided in some cases. The existence of a complex is deduced from the analysis of some change in the absorption spectrum of the individual components. However, as Person points out (53), the criterion for the existence of a complex is not the appearance of a new absorption band but rather that the new absorption band can be analyzed to give a single, non-zero, value for  $K$  and a finite, constant value of  $\epsilon$ .

A detailed discussion of the difficulty in obtaining accurate values of  $K$  for the various procedures will not be given; however the basic experimental necessity is that the concentration of complex must be of the same order of magnitude as the equilibrium concentration of the most dilute component (53). It is usually necessary to run some preliminary semi-quantitative experiments and find approximate values of  $K$  and  $\epsilon$  so that concentrations can be found that establish this condition. If this is not done the errors in the value of  $K$  will be so large as to make it virtually impossible to tell if  $K$  is different from zero - especially for weak interactions.

## EXPERIMENTAL

## A PURIFICATION OF CHEMICALS

1. Chloroform: Some difficulty was experienced in purifying suitable chloroform for use as a solvent in this work. The Fisher U.S.P. chloroform that was used for purification contains approximately 0.75% ethanol as a preservative. This ethanol would interfere with the kinetic data as the rates of chlorination are strongly affected by the polarity of the medium. Once this ethanol is removed, however, the chloroform decomposes rapidly under the influence of light and oxygen to form phosgene. (9, 27, 70).

Initially the method of Fieser was used as a purification (26). The chloroform was washed twice with concentrated sulphuric acid, washed several times with water, dried over  $\text{CaSO}_4$ , and distilled in the dark. The stability of the chloroform was always checked just before use by testing with KI, a positive test indicating phosgene (actually a peroxide (27) which then decomposes to form phosgene). This method of purification is not very satisfactory because the chloroform will not remain stable for very long. However all rate runs in pure chloroform and all those with the salts tetrabutylammonium chloride, N-ethylpiperidine hydrochloride, tetrabutylammonium perchlorate, and pyridine hydrochloride were obtained with

chloroform purified by this method just before use.

An alternative procedure, which is much more satisfactory, was used in the later stages of this work. The chloroform was washed twice with concentrated  $H_2SO_4$ , distilled in the dark, and stored over chromatographic alumina. It would then be filtered just before use. Chloroform stored over alumina seems to be stable for an almost indefinite length of time (at least three weeks). All of the equilibrium constant data and the rate runs with HCl were obtained using this chloroform.

2. Acetic Acid: Acetic acid was purified by a method similar to that of Orton and Bradfield (50). Commercial acetic acid was refluxed approximately 3 hours with  $CrO_3$  (2 gm./100 cc. of acid) and then distilled off the  $CrO_3$ . The freezing point was then taken using a calibrated Beckman Thermometer and the depression from the literature value of  $16.63^\circ C$  (68) taken as a measure of the amount of water in the acetic acid. The calculated amount of acetic anhydride was then added and the mixture was refluxed for an hour. The acetic acid was then distilled through a four foot by  $3/4$  inch diameter column packed with glass helices. Boiling point at 740 mm. pressure:  $116.0 - 116.5^\circ C$ . Freezing point:  $16.51^\circ C$ .

3. p-Chloroanole: Eastman p-chloroanisole was purified by distillation through an Wheeler "All-Glass" GE-125-2H fractionating column rated at better than 90



theoretical plates as determined by an n-heptane: methylcyclohexane mixture,  $\alpha$  equal to 1.07. The boiling point of the collected fraction was 89.0°C at P= 21 mm. The pressure was controlled to  $\pm 1$  mm. by the apparatus shown in Figure I.

4. Chlorine: Chlorine gas was taken directly from a cylinder ( C.I.L.) and passed through two sulphuric acid bubblers before use. All chlorine solutions were prepared by first making a saturated solution of chlorine in the solvent and then diluting to the required concentration.

5. Hydrogen Chloride: Hydrogen chloride gas was used directly from a cylinder (Matheson).

6. Benzene: Commercial benzene was purified by the method of Fieser (26). Fraction collected 79.5 - 80.0° C.

7. Toluene: Commercial toluene was purified by the method of Fieser (26). Fraction collected 109 - 110° C.

8. Eastman 2,4- dichloroanisole and B.D.H. chlorobenzene were used without further purification for the gas chromatography work.

## B. PREPARATION OF CHEMICALS

1. Tetrabutylammonium chloride: This salt was prepared essentially by the method of Umni, Elias, and Schiff. (66). Silver chloride was prepared by mixing equimolar quantities of aqueous solutions of NaCl and AgNO<sub>3</sub> in the dark. The precipitated AgCl was filtered under vacuum,

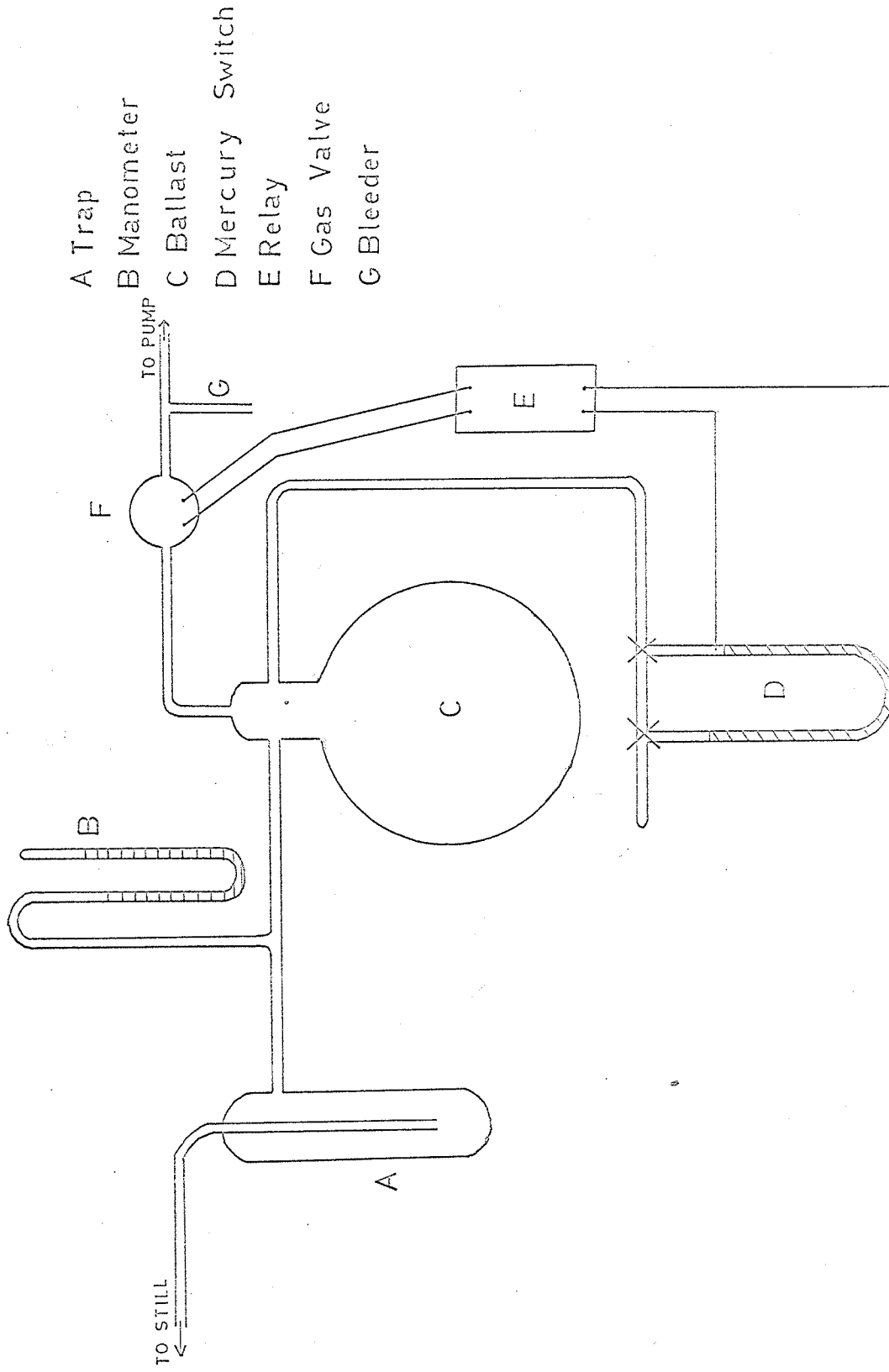


FIG. I

washed with water, and washed once with absolute methanol. A 10% excess of the AgCl was added to 200 cc. of a 1.1 Molar solution of tetrabutylammonium iodide (Eastman) in methanol. The solution was left to stand for two days in the dark and then the precipitated AgI was filtered. The methanol was evaporated from the filtrate and the tetrabutylammonium chloride crystallized as a glassy solid. It was then recrystallized three times from acetone, dried in an Abderhalden drying pistol with  $P_2O_5$  and refluxing acetone for about two weeks and finally transferred to a vacuum desiccator with  $P_2O_5$ .

Melting Point: 74.2-75.6

Literature: 52 - 54 (44)

75 (66)

74.0-74.5 (14)

92.5-94.2 (1)

Chloride Analysis: 12.62% (By potentiometric  $AgNO_3$  titration).

Calculated Value: 12.76%

2. Pyridine Hydrochloride: Pyridine hydrochloride was prepared by passing cylinder HCl gas through a solution of 75 gm. of pyridine (Matheson Karl Fischer Reagent) in 100 ml. of dry ether. The precipitated pyridine hydrochloride was filtered and washed with 50 ml. of ether. The salt was recrystallized twice from 2-propanol and then dried in a vacuum desiccator with  $P_2O_5$ .

Melting Point: 141.2 - 144.2    Literature: 143.4 (65)  
144.5 (28)

Chloride Analysis: 30.56% (Potentiometric  $\text{AgNO}_3$  titration)  
Calculated Value: 30.66%

3. Tetrabutylammonium Perchlorate: Tetrabutylammonium iodide, 3.7 gm. (0.01 Moles) in 20 ml. of methanol, and  $\text{AgClO}_4$ , 2.1 gm. (0.01 Moles) in 20 ml. of methanol, were mixed for approximately 5 minutes. The  $\text{AgI}$  was filtered from the solution and then the methanol was evaporated from the filtrate. The salt was recrystallized three times from ethyl acetate and dried over  $\text{P}_2\text{O}_5$  in a vacuum desiccator.

Melting Point: 213.2 - 214.0°C.    Literature: 207-209 (24)  
213.3 (31)

4. N-Ethylpiperidine Hydrochloride: Eastman N-ethylpiperidine was distilled and the fraction boiling at 129.0 - 130.2°C was collected. Twenty milliliters of this N-ethylpiperidine was dissolved in 50 ml. of anhydrous ether and then  $\text{HCl}$  gas was passed through the solution. The solution was cooled in an ice bath, the precipitated N-ethylpiperidine hydrochloride filtered, washed once with ether and then transferred to a vacuum desiccator. The crude product was crystallized from a 3:1 mixture of ligroin (b.p. 60 - 80°C) and 2-propanol, and then dried over  $\text{P}_2\text{O}_5$  in a vacuum desiccator.

Melting Point: 231 - 233°C.    Literature: 224 - 225°C. (38)

## C CHLORINATION OF BENZENE: COHEN'S METHOD

Several attempts were made to duplicate Cohen's method (16) for the preparation of chlorobenzene from benzene in the presence of pyridine. An excerpt from this paper is reprinted below.

Chlorine was passed into 50 grams of benzene containing a few drops of pyridine, and the mixture was warmed to 50°C. The action proceeded rapidly with the evolution of hydrogen chloride. The product was shaken with alkali, dehydrated, and distilled. Some unchanged benzene and a little dichlorobenzene were separated. The yield of pure chlorobenzene was 30 gms.

Unfortunately there are very few experimental details. No indication of the purity or source of the benzene and chlorine is given. It is difficult to tell whether chlorine was passed continuously through the reaction mixture or whether a saturated solution was prepared which was then allowed to react. However the approximate solubility of chlorine in benzene is 1.4 Molar at room temperature as determined by iodine-thiosulphate titrations. Since benzene itself is 11.1 Molar in benzene the yield would be expected to be only about 12% chlorobenzene. Cohen implies that, in his method, very little benzene

was left, although the yield of pure chlorobenzene was only 42%. At any rate the high yields indicate that chlorine was passed continuously through the benzene-pyridine mixture.

As a result of these conclusions, the first method used in the attempts to duplicate Cohen's procedure was by passing chlorine continuously through the purified benzene-pyridine mixture in a flask immersed in a constant temperature oil bath at  $60 \pm 1^\circ\text{C}$ . No attempt was made to shield the flask from room light although immersion in the oil bath should screen the mixture quite effectively. Reactions with benzene and with benzene-pyridine mixtures (ratio of 75:1 by volume of benzene to pyridine) were attempted. The products were analyzed by distillation. However the only products obtained were benzene and a white solid which was left as a residue in the distilling flask. The yield of this solid varied considerably from just trace amounts to as much as 5.5 gm. from 100 gm. of benzene after four hours reaction time. The solid formed in cases where pyridine was present as well as in pure benzene. On two recrystallizations of the solid from ethanol a white crystalline compound was obtained which was identified as  $\alpha$ -benzenehexachloride by melting point,  $154.6 - 156.8^\circ\text{C}$ ; literature value  $158.5 - 159.5$  (2); and infra red spectrum in  $\text{CS}_2$ (2).

In view of the failure of this method a second method was attempted where a saturated solution of chlorine

in benzene or benzene-pyridine mixture was prepared. The reaction vessel was wrapped in aluminum foil in order to minimize the photochemical addition reaction of chlorine to benzene to form  $\alpha$ -benzenehexachloride (30, 46) and then immersed in a constant temperature oil bath at  $60 \pm 1^\circ\text{C}$ . Samples were withdrawn from the reaction mixture and analyzed by gas chromatography using a Burrell Model K-3 gas chromatograph with an Apiezon-L column. The conditions for the analysis were: injection temperature,  $140^\circ\text{C}$ ; column temperature,  $137^\circ\text{C}$ ; detector temperature,  $100^\circ\text{C}$ ; flow rate of helium, 43 cc/min. The ratio of benzene to chlorobenzene was determined by comparison of peak heights with those for known standard mixtures. No estimation of the amount of  $\alpha$ -benzenehexachloride could be obtained in the analysis. The results are given in Table I.

#### D REACTION RATE MEASUREMENTS

##### 1. p-Chloroanisole in Chloroform

All reaction rates in chloroform were measured on a Beckman Model D.K. -1 spectrophotometer, essentially by the method of Andrews and Keefer (37). The cell housing was controlled at  $25.0 \pm 0.2^\circ\text{C}$  by circulating water from a constant temperature bath. The chlorine content of the reaction mixture as a function of time was determined by following the changes in absorbance at a wavelength between 330 and 400  $\text{m}\mu$  chosen so as to give initial absorbance values between 0.5 and 1.0.

TABLE I

GAS CHROMATOGRAPHIC ANALYSIS OF SAMPLES FROM THE  
 CHLORINATION OF BENZENE: COHEN'S METHOD.

$t=60^{\circ}\text{C}$

Benzene Vol.(cc.)	Pyridine Vol.(cc.)	Time (hours)	$\frac{\text{Moles C}_6\text{H}_5\text{-Cl}}{\text{Moles C}_6\text{H}_6}$
5.0	-	19	0.005
5.0	-	18.5	0.005
8.0	0.1	5.5	0.10
8.0	0.2	6.0	0.09

The spectrophotometric method of measurement was chosen in preference to the iodine-thiosulphate volumetric method because it was found to be very difficult to obtain accurate titration values. Apparently this problem is the consequence of the heterogeneous quenching mixture (63). Before the chlorine is destroyed by the KI quenching solution, the traces of water introduced into the chloroform greatly accelerate the reaction between chlorine and aromatic.



Before any rate runs were attempted, a check of the stability of a solution of chlorine in chloroform was made. A  $5.47 \times 10^{-2}$  molar solution of chlorine gave both a constant absorbance value at  $370\text{m}\mu$  and a constant titration value over a 24-hour period.

Two procedures were followed in preparing samples for a reaction run. However in all cases the work was done, as much as possible, in subdued light to prevent photodecomposition of chloroform or any photochemical reaction of the chlorine with either chloroform or the aromatic substrate. In the first method, used for slow reactions, stock solutions of chlorine and the aromatic were mixed in a volumetric flask in the constant temperature bath. A sample was then withdrawn for the spectrophotometer cuvette and placed directly in the instrument. In the second method, used for faster reactions, 2 ml. and 1 ml. aliquots of the aromatic and chlorine solutions were mixed in the cuvette which was already in the spectrophotometer. Although temperature control is probably not as good for the first few minutes reaction by this method, it enables earlier readings to be obtained for fast runs.

The rate runs were generally followed to greater than 75% reaction except in the cases of p-chloroanisole in chloroform with no added salts where only initial rates were needed. The measured absorbances were corrected for the small absorbances, (never greater than 0.05) due to the salts. The initial chlorine concentration was usually obtained by titration of an

aliquot from the stock solution. However in some cases the value was estimated from the initial absorbance value, although this method does not give very satisfactory results because absorbance is affected by the concentration and nature of other reagents in the solution (see results section, page 38, for further discussion of this factor). In runs with HCl the concentration of acid was determined by withdrawing samples from the cuvette after the reaction and titrating with standard NaOH using phenolphthalein as indicator.

## 2. Toluene in Acetic Acid

The kinetic measurements in acetic acid were carried out by analyzing for unreacted chlorine iodometrically. All rate measurements were performed in a darkened room in a constant temperature bath of  $25.0 \pm 0.1^\circ \text{C}$ . Experiments were started by mixing, in a glass-stoppered volumetric flask, solutions of known chlorine and known aromatic (or aromatic and salt) concentration. Zero time was established by withdrawing an aliquot from the reaction mixture never later than four minutes after mixing. The runs were followed to 75 - 80% completion by taking five to seven samples for each kinetic experiment.

A check of the stability of chlorine in acetic acid was also made and negligible decrease in the chlorine concentration occurred over five hours which is longer than any of the kinetic runs in acetic acid.

## E PRODUCT ANALYSIS FOR p-CHLOROANISOLE IN CHLOROFORM

The product analysis for the chlorination of p-chloroanisole in chloroform was carried out by gas chromatography with a 30% Apiezon-L on Chromosorb-W column. Conditions for the analysis were; injection temperature, 190°C; column temperature, 180°C; detector temperature, 105°C; helium flow rate, 50 cc./min.. The only product obtained was 2,4-dichloroanisole which was identified by comparison of its retention time with known samples. The retention times for the two compounds were: p-chloroanisole, 9.6 min.; 2,4-dichloroanisole, 22.2 min. The concentration of the injected samples was determined from comparison of peak areas with those for known samples using an integrating recorder.

The product analyses were carried out by preparing a solution of p-chloroanisole in chloroform and adding a solution of chlorine in chloroform. The chlorine concentration was higher than that used in the rate runs in order to obtain a significant amount of product for the analyses. The reaction mixture was allowed to stand in the dark for at least 10 half lives and then samples were injected directly into the chromatograph. The large solvent chloroform peak did not interfere with the analyses

The results are shown in Table II.

TABLE II

GAS CHROMATOGRAPHIC PRODUCT ANALYSIS FOR THE CHLORINATION  
OF P-CHLOROANISOLE IN CHLOROFORM.

Initial p-Cl Anisole (Moles/lit.)	Salt (1) (moles/lit.)	Final p-Cl Anisole (Moles/lit.)	Final 2,4-diCl Anisole (moles/lit.)	Yield %
$10.9 \times 10^{-2}$	-	$5.0 \times 10^{-2}$	$4.1 \times 10^{-2}$	84
$14.4 \times 10^{-2}$	-	$9.4 \times 10^{-2}$	$3.4 \times 10^{-2}$	89
$21.2 \times 10^{-2}$	$3.51 \times 10^{-2}$	$14.7 \times 10^{-2}$	$6.2 \times 10^{-2}$	99
$17.0 \times 10^{-2}$	$2.81 \times 10^{-2}$	$8.7 \times 10^{-2}$	$7.8 \times 10^{-2}$	97

(1) The salt used was tetrabutylammonium perchlorate.

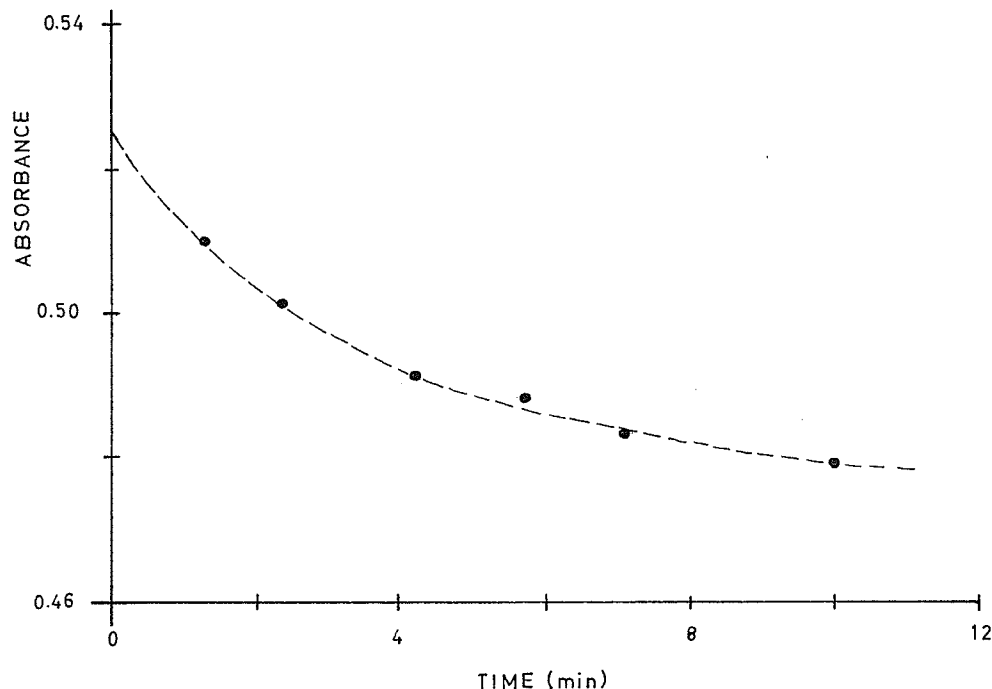
#### F EQUILIBRIUM CONSTANT MEASUREMENT

All preliminary data for the equilibrium constants were obtained using a Beckman D.K. - 1 spectrophotometer. Solutions of various concentrations of tetrabutylammonium chloride and chlorine in chloroform were scanned in order to find the best experimental conditions for determining the equilibrium constant.

The actual experimental measurements were obtained using a Beckman D.U. spectrophotometer thermostated at  $25.0 \pm 0.1^\circ \text{C}$ . by circulating water from a constant temperature bath.

Under the conditions of the determination with high tetrabutylammonium chloride (T.B.A. Cl will be used as an abbreviation) concentrations ( $3.2 \times 10^{-2}$  M. to  $16.8 \times 10^{-2}$  M.) and low chlorine concentrations ( $4.5 \times 10^{-4}$  M.) it was found that a solution of chlorine and T.B.C. Cl was unstable with time. However this difficulty was avoided by taking the measurements fairly quickly by the following procedure. A stock solution of T.B.A. Cl was prepared and 2 ml. of the solution pipetted into the cuvette which was then placed in the spectrophotometer. 1 ml. of a stock chlorine solution was then added and absorbance measurements taken over a time of approximately twenty minutes. These values were then extrapolated back to zero time to obtain the initial absorbance value. An example of an extrapolation is shown in Figure II. The error in this extrapolated value of absorbance is, of course, larger than would be expected for normal readings on stable solutions. A solution of  $10 \times 10^{-2}$  M. T.B.A. Cl and 4.0 and  $10^{-2}$  M. Chlorine gave extrapolated values at  $305_{m\mu}$  of 0.525, 0.538, and 0.516 on three separate determinations. At lower salt concentrations, where the change with time is slower, the values would have better precision but at higher salt concentrations the precision would be worse. For simplification the error in all the absorbance values was estimated at  $\pm 3\%$ .

FIG. II A plot of Absorbance versus Time for a solution of tetrabutylammonium chloride (0.10 M.) and chlorine ( $4.0 \times 10^{-4}$  M.) to show the method of extrapolation to zero time.



Although temperature control will probably be less consistent than  $\pm 0.1^\circ\text{C}$  by this method it should still be as good as  $\pm 0.5^\circ\text{C}$ , even for the first few minutes after mixing. However this poor temperature control, along with the error in pipetting 1 and 2 ml. aliquots into the cuvettes, will make the experimental error even larger than the  $\pm 3\%$  predicted from the absorbance values. The total error has therefore been estimated as  $\pm 5\%$ .

The chlorine concentration of the complex mixtures was determined by measuring the absorbance of a

stock solution of chlorine in chloroform at  $305\text{ m}\mu$   
(absorptivity of chlorine in chloroform at  $305\text{ m}\mu$  is  $54.4$   
 $\text{lt.mole}^{-1} \text{ cm}^{-1}$  as determined by iodimetric methods).  
The stock solution was then diluted to the concentration  
necessary for the complex mixture.

## RESULTS

## I KINETICS

## A CHLORINATION OF P-CHLOROANISOLE IN CHLOROFORM

It was assumed from previous literature results (page 4) that the chlorination of p-chloroanisole in chloroform would be first order in chlorine and first order in aromatic substrate. The rate equation for the reaction would then be

$$-\frac{d(\text{Cl}_2)}{dt} = k_A(\text{ArH})(\text{Cl}_2) \quad (1)$$

where  $k_A$  is the rate constant in litre mole<sup>-1</sup> sec<sup>-1</sup>.

In order to simplify the kinetic work all runs were carried out with the p-chloroanisole in large excess of the chlorine. The p-chloroanisole concentration will remain effectively constant throughout a kinetic run and the rate equation 1 can be simplified to

$$-\frac{d(\text{Cl}_2)}{dt} = k(\text{Cl}_2) \quad (2)$$

where  $k = k_A(\text{ArH})$ . This is now a "pseudo" first order rate equation and can be easily integrated.

All of the rate data in chloroform were obtained by following the chlorine concentration by absorbance measurements. In the general case Beer's Law predicts that

$$A = \epsilon(\text{Cl}_2) \quad (3)$$



where  $A$  is the absorbance  
 $\epsilon$  is the absorptivity  
 $l$  is the cell thickness in centimeters

Since in a given run at some fixed wavelength  $\epsilon$  and  $l$  are constant

$$A = a (Cl_2) \quad (4)$$

where  $a = \epsilon l$ . Substituting equation 4 into equation 2 gives

$$-\frac{d}{dt}\left(\frac{A}{a}\right) = k\left(\frac{A}{a}\right) \quad (5)$$

Since  $a$  is a constant it can be factored out of both sides of equation 5

$$-\frac{d}{dt}(A) = kA \quad (6)$$

Integration of equation 6 gives

$$-\ln A = kt + I' \quad (7)$$

where  $I'$  is the integration constant. Converting equation 7 to base 10 logarithms for convenience gives

$$-\log A = \frac{kt}{2.3} + I \quad (8)$$

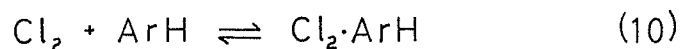
Equation 8 was used to handle all the data that was first order in chlorine by the graphical method of plotting  $-\log A$  versus time. This should give a straight line of slope  $m = \frac{k}{2.3}$  and an intercept of  $I$ . Since  $k$  was defined

as  $k_A$  (Ar H) the rate constant can then be obtained from the expression

$$k_A = \frac{2.3 m}{(ArH)} \quad (9)$$

This method of determining rate constants depends on the fact that the chlorine concentration is directly proportional to the absorbance of the solution as defined by equation 4. However throughout the course of the experimental work it was found that a solution of a given chlorine concentration would give a different absorbance value depending on the nature and concentration of other reagents in the solution such as p-chloroanisole or the chloride salts. Therefore it should be shown that, although the constant  $a$  in equation 4 may vary from run to run, in any given run it will remain constant.

Suppose there is a solution of p-chloroanisole and chlorine in chloroform and that the two interact to form a 1:1 charge transfer complex of the type discussed by Andrews and Keefer (4). The following equilibrium will be set up



The total chlorine concentration,  $(Cl_2)_T$ , would be given by

$$(Cl_2)_T = (Cl_2)_F + (Cl_2 \cdot ArH) \quad (11)$$

where  $(Cl_2)_F$  refers to the concentration of uncomplexed chlorine. Now the absorbance of the solution would be

given by

$$A = \epsilon_{\text{Cl}_2}(\text{Cl}_2) + \epsilon_{\text{Cl}_2\text{ArH}}(\text{Cl}_2\cdot\text{ArH}) \quad (12)$$

assuming that p-chloroanisole does not absorb appreciably at the wavelength under consideration. However, from the equilibrium in equation 10, K is given by

$$K = \frac{(\text{ArH}\cdot\text{Cl}_2)}{(\text{ArH})(\text{Cl}_2)} \quad (13)$$

Simultaneous solution of equations 11, 12, and 13 gives the following results

$$A = \left[ \frac{\epsilon_{\text{Cl}_2} + K\epsilon_{\text{ArH}\cdot\text{Cl}_2}(\text{ArH})}{1 + K(\text{ArH})} \right] (\text{Cl}_2)_T \quad (14)$$

$$A = \left[ \epsilon_{\text{Cl}_2} + K\epsilon_{\text{ArH}\cdot\text{Cl}_2}(\text{ArH}) \right] (\text{Cl}_2)_F \quad (15)$$

In other words, if chlorine forms a 1:1 complex with p-chloroanisole, the changes in absorbance of a given solution of chlorine for different concentrations of aromatic, will not affect the relationship that absorbance is still directly proportional to chlorine concentration. This means that a modified form of Beer's Law still applies although the value of the absorptivity,  $\epsilon$ , will be dependent on the concentration of p-chloroanisole. Other complexing agents such as the chloride salts will also give a similar result.

The importance of this fact lies in the use of spectrophotometric techniques for determining reaction rates where the absorbance of a chlorine solution must be proportional to chlorine concentration as in equation 4 if meaningful kinetic data are to be obtained. It appears from this derivation that such a condition will still exist even in the presence of such complexing agents as p-chloroanisole and the halide salt catalysts.

1. Pure Chloroform: The results for a typical run for the chlorination of p-chloroanisole in chloroform at 25.0° C are shown in Table III with the plot of  $-\log A$  versus time in Figure II.

Since the rate data did not seem to obey the "pseudo" first order relationship as predicted by equation 6 and equation 8 an attempt was made to evaluate a rate constant from the initial slope of the first order plots. It was found, however, to be difficult to estimate the initial slopes of these curves and so a somewhat arbitrary assumption was made that the plots were linear for the first 10% reaction. The best straight line was then drawn through these points. This assumption proved to be quite good in most cases and a typical example is shown in Figure III. Table IV lists the rate constants obtained by this method of initial slopes.

Although there is quite a scatter in the rate constants, they are relatively constant over a wide range of

TABLE III

CHLORINATION OF P-CHLOROANISOLE IN CHLOROFORM  
 $t=25^{\circ}\text{C}$ 

Initial conditions: p-chloroanisole 0.947 M.  
chlorine  $6.1 \times 10^{-2}$  M.

Time (min.)	Absorbance	-Log A
5	0.945	0.025
10	0.897	0.047
15	0.842	0.075
20	0.780	0.108
25	0.715	0.146
30	0.651	0.186
35	0.581	0.236
40	0.515	0.288
45	0.449	0.348
50	0.387	0.412
55	0.333	0.478
60	0.281	0.551
65	0.336	0.627
70	0.196	0.708
75	0.163	0.788
80	0.133	0.876

FIG. II A plot of the experimental data of Table III, showing a typical example of the chlorination of p-chloroanisole in chloroform at 25°C.

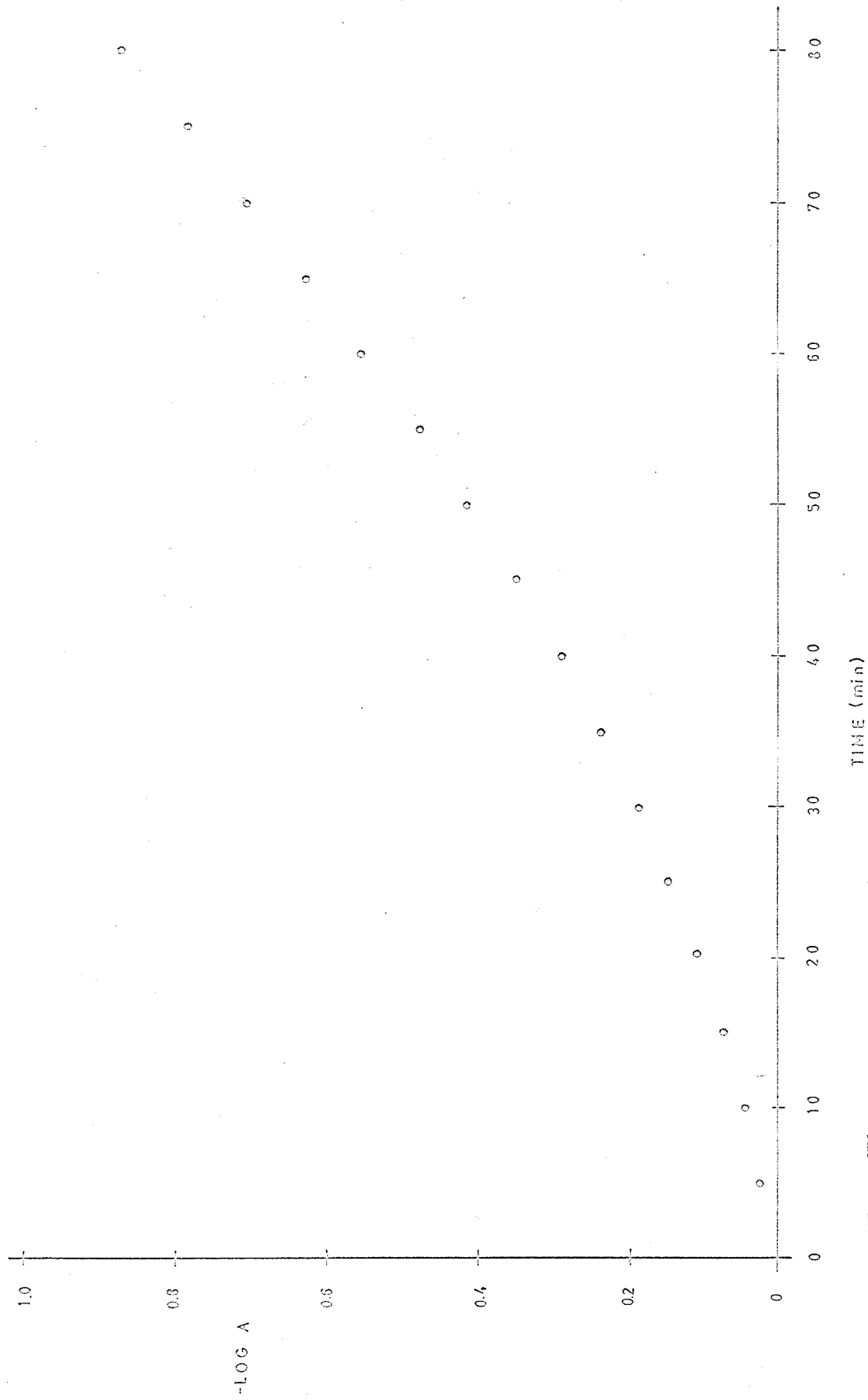


FIG. II

FIG. III An example of the graphical method of obtaining the second order rate constant,  $k_A$ , from the initial slope of the  $-\log A$  versus Time plot for the chlorination of p-chloroanisole in chloroform.

Chlorine  $3.32 \times 10^{-2}$  M.

p-chloroanisole 0.946 M.



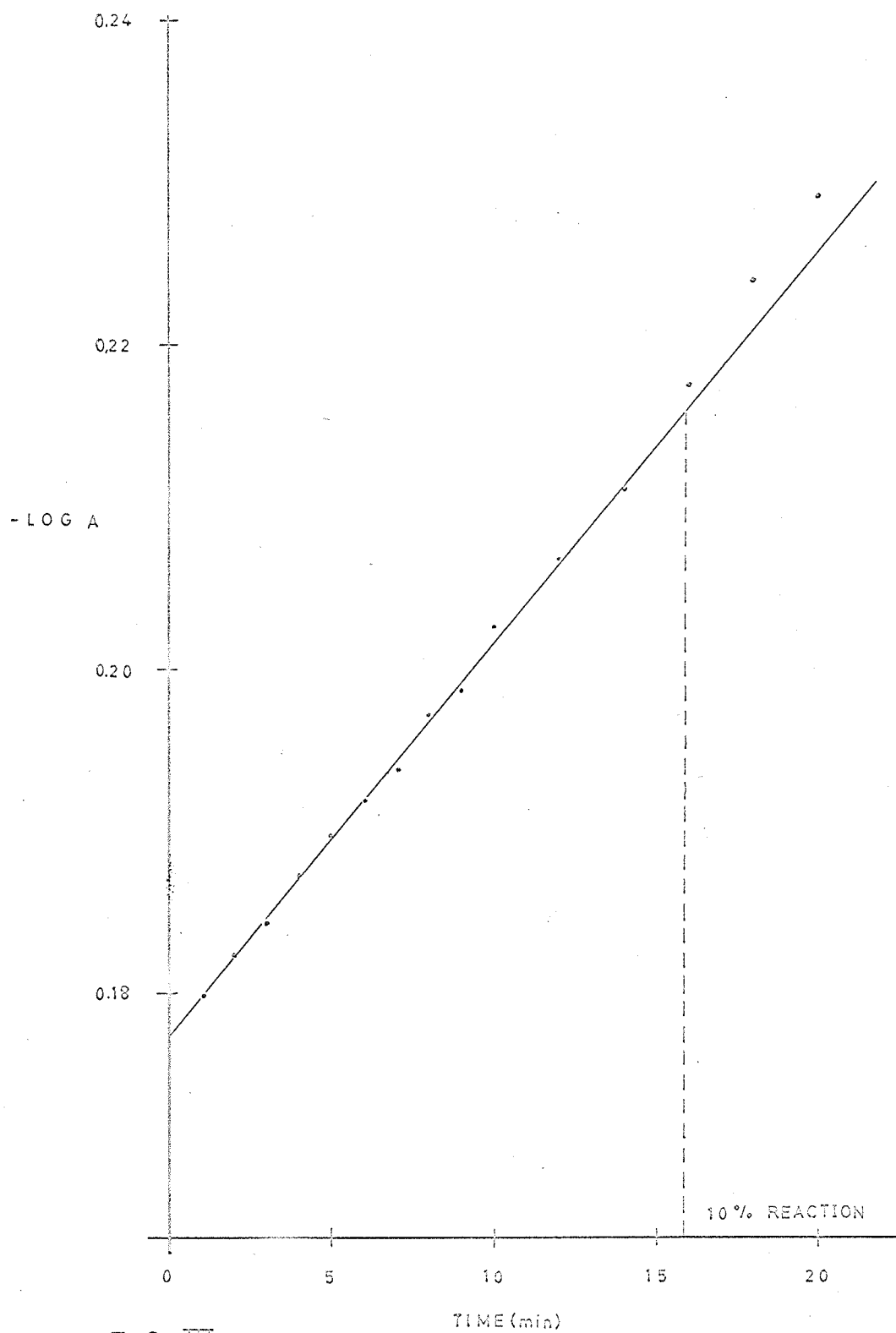


FIG. III

TABLE IV

SECOND ORDER RATE CONSTANTS,  $k_R$ , FOR THE CHLORINATION OF  
 p-CHLOROANISOLE IN CHLOROFORM  
 $t=25^\circ\text{C}$

(ArH) Moles/liter	(Cl <sub>2</sub> ) × 10 <sup>2</sup> Moles/liter	$k_R \times 10^4$ Liter mole <sup>-1</sup> sec. <sup>-1</sup>
1.445	2.1 <sup>(1)</sup>	1.05
1.335	1.6 <sup>(1)</sup>	0.93
1.298	1.85	1.11
1.285	1.33	1.03
1.010	3.7 <sup>(1)</sup>	1.03
0.946	3.32	0.98
0.946	3.27	0.98
0.946	3.22	0.93
0.909	3.20	1.13
0.900	2.30	1.00
0.864	2.9 <sup>(1)</sup>	1.06
0.578	5.3 <sup>(1)</sup>	0.96
0.519	4.50	1.09
0.494	4.1 <sup>(1)</sup>	0.93

(1) These chlorine concentrations were estimated from initial absorbances and are not as reliable as those obtained from iodimetric methods because the absorbance is dependent on the concentration of aromatic (See RESULTS, Section I)

aromatic concentration. The second order rate constant,  $k_A$ , given by equation 1 is therefore  $1.01 \pm 0.07 \times 10^{-4} \text{ lt. mole}^{-1} \text{ sec}^{-1}$ .

2. Chloroform with HCl: Rate data were obtained for the chlorination of p-chloroanisole in chloroform in the presence of added HCl. The HCl concentration was kept in large excess of the initial chlorine concentration so that HCl released as one of the products of the reaction did not alter the concentration appreciably. The rate data was found to obey the expression

$$-\frac{d(\text{Cl}_2)}{dt} = k_B (\text{ArH})(\text{Cl}_2)(\text{HCl}) \quad (16)$$

where  $k_B$  is the third order rate constant in  $\text{lt.}^2 \text{ mole}^{-2} \text{ sec}^{-1}$ . Again since both

$$(\text{ArH}) \gg (\text{Cl}_2)$$

$$(\text{HCl}) > (\text{Cl}_2)$$

$$-\frac{d(\text{Cl}_2)}{dt} = k (\text{Cl}_2)$$

where  $k = k_B (\text{ArH}) (\text{HCl})$

Equation 8 was again used to evaluate the rate constants and good linear plots were obtained to at least 75% reaction. A typical plot of  $-\log A$  versus time is shown in Figure IV and the results are listed in Table V. The value of  $k_B$  is therefore  $1.43 \pm 0.05 \times 10^{-2} \text{ lt.}^2 \text{ mole}^{-2} \text{ sec}^{-1}$ .

FIG. IV A plot of  $-\text{Log } A$  versus Time for the chlorination of p-chloroanisole in chloroform with added HCl.

Chlorine  $5.74 \times 10^{-3}$  M.

p-chloroanisole 0.142 M.

Hydrogen Chloride  $4.34 \times 10^{-2}$  M.

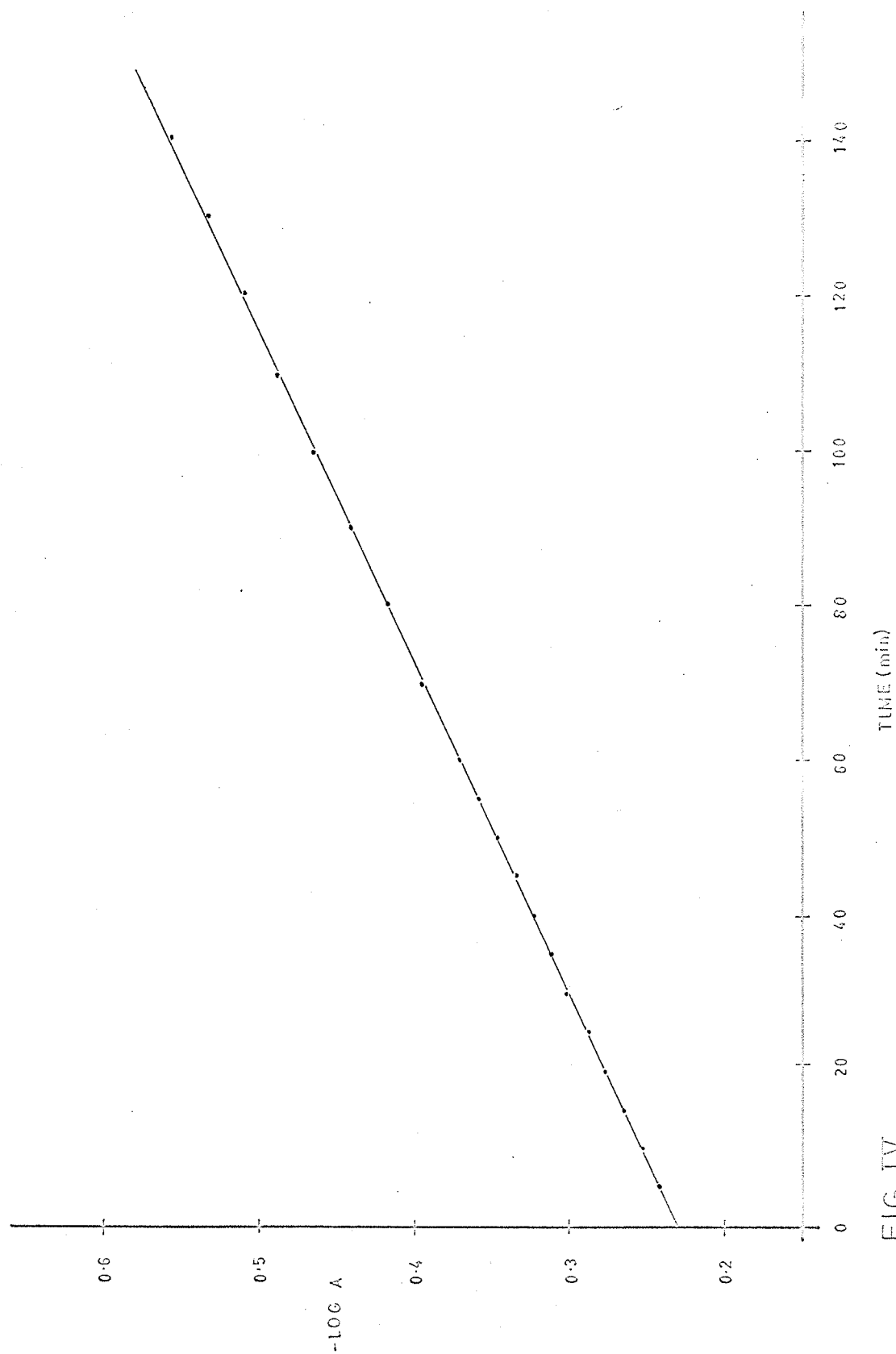


FIG. IV

TABLE V

## CHLORINATION OF p-CHLOROANISOLE IN CHLOROFORM

## WITH HYDROGEN CHLORIDE

t=25°C

(ArH) Moles/lit.	(Cl <sub>2</sub> ) × 10 <sup>3</sup> Moles/lit.	(HCl) × 10 <sup>2</sup> Moles/lit.	k <sub>B</sub> × 10 <sup>2</sup> Lt. <sup>2</sup> mole. <sup>-2</sup> sec. <sup>-1</sup>
0.283	2.87	8.79	1.50
0.142	5.74	4.34	1.45
0.344	2.89	5.42	1.36
0.274	2.70	7.06	1.36
0.167	2.70	3.85	1.45

Because HCl is one of the products of the reaction between chlorine and p-chloroanisole it was thought that for the reaction in pure chloroform the data could be explained by a combined rate expression using equation 1 and equation 16.

$$-\frac{d(\text{Cl}_2)}{dt} = k_A(\text{ArH})(\text{Cl}_2) + k_B(\text{ArH})(\text{Cl}_2)(\text{HCl}) \quad (17)$$

Integrating equation 17 and using the usual assumption that chlorine concentration is directly proportional to absorbance gives

$$-2.3 \text{ Log } A = (ArH) \left[ k_A + k_B(\text{HCl}) \right] t + I \quad (18)$$

Using the known values of  $k_A = 1.01 \times 10^{-4} \text{ lt. mole}^{-1} \text{ sec.}^{-1}$  and  $k_B = 1.43 \times 10^{-2} \text{ lt.}^2 \text{ mole}^{-2} \text{ sec.}^{-1}$  and experimental values of  $(ArH)$ ,  $(\text{HCl})$ ,  $\text{log } A$ , and time from a kinetic run, the left hand side of equation 18 can be plotted against the right hand side and a straight line should result. The HCl concentrations were obtained from the initial chlorine concentration and the percent reaction at any time since one mole of HCl is produced for every mole of chlorine that reacts. The result of this procedure (for the same run as shown in Table III and Figure II) are shown in Table VI and the graph of equation 18 is plotted in Figure V.

3. Chloroform with Added Salts: A number of chlorination reactions were carried out in the presence of the added salts pyridine hydrochloride, tetrabutylammonium chloride, tetrabutylammonium perchlorate, and N-ethylpiperidine hydrochloride. In all cases the salt was in large excess of the chlorine concentration.

The reactions were all found to be first order in chlorine so that plots of  $\text{log } A$  versus time as in equation 8 gave a good straight line for at least 75% reaction.

TABLE VI

COMBINED RATE EXPRESSION FOR THE CHLORINATION OF  
p-CHLOROANISOLE IN CHLOROFORM

$$-\frac{d(\text{Cl}_2)}{dt} = k_A(\text{ArH})(\text{Cl}_2) + k_B(\text{ArH})(\text{Cl}_2)(\text{HCl})$$

Initial conditions: p-chloroanisole 0.945 M.  
chlorine  $6.1 \times 10^{-2}$  M.

Time (Sec.)	HCl $\times 10^2$ (Moles/lit.)	$[k_B(\text{ArH})(\text{HCl}) + k_A(\text{ArH})] \times 10^5$ (Sec.)	$[k_B(\text{ArH})(\text{HCl}) + k_A(\text{ArH})]t$ $\times 10^2$	-Log A
300	0.33	14.0	4.2	0.025
600	0.62	17.9	11.3	0.047
900	0.95	22.3	20.2	0.075
1200	1.33	27.4	33.0	0.108
1500	1.72	32.7	49.1	0.146
1800	2.11	38.0	68.4	0.186
2100	2.54	43.8	92.2	0.236
2400	2.97	49.6	119	0.288
2700	3.34	54.6	147	0.348
3000	3.71	59.6	179	0.412
3300	4.04	64.0	211	0.478
3600	4.35	68.2	246	0.551
3900	4.62	71.7	280	0.627
4200	4.86	75.2	316	0.708
4500	5.06	77.0	351	0.788
4800	5.25	80.4	386	0.876



FIG. V A plot of the experimental data from Table VI.

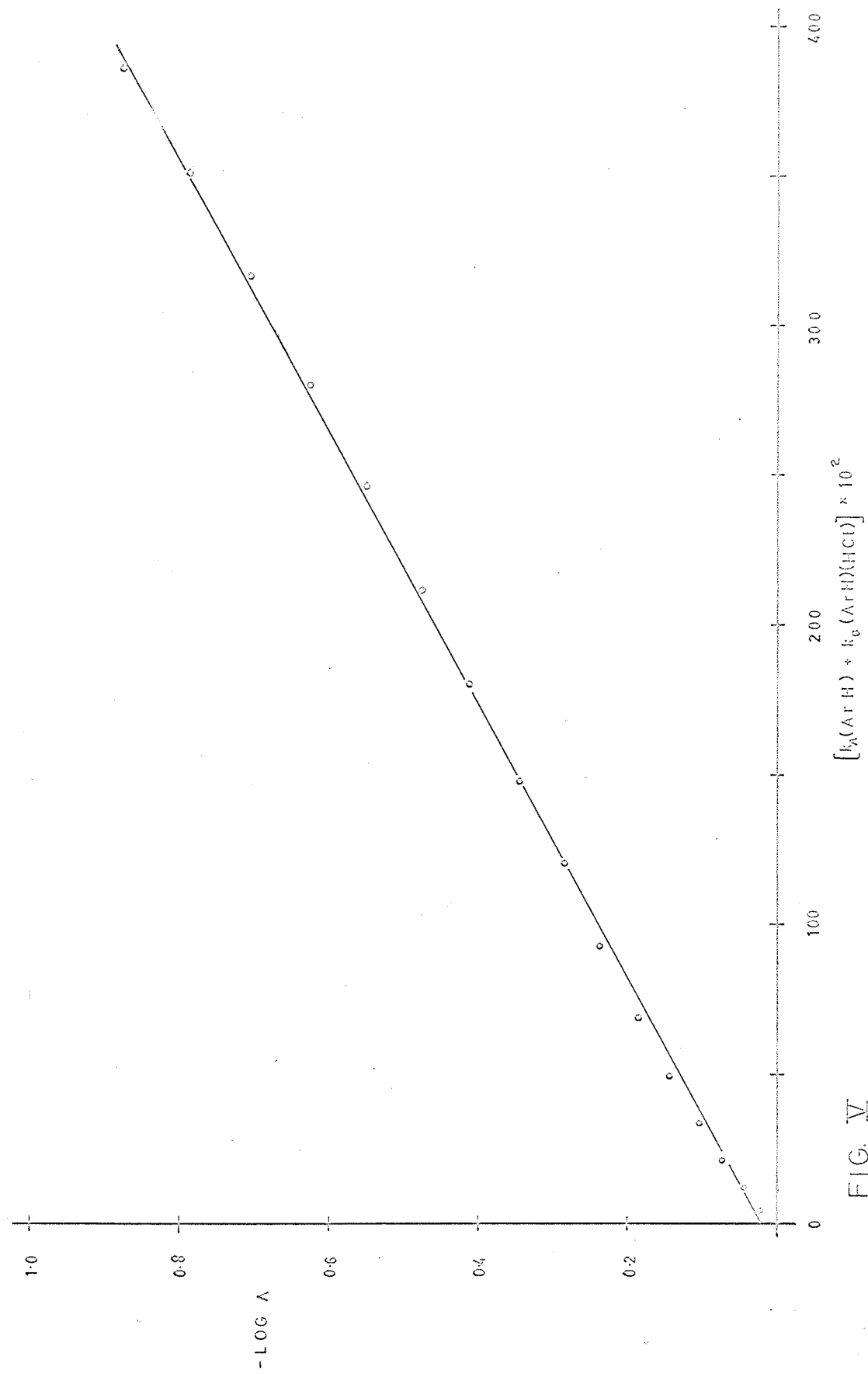


FIG. V

Some runs with tetrabutylammonium chloride where the salt was not as much as five times the initial chlorine concentration deviated from linearity sooner than 75% reaction. It was assumed that the reactions were first order in p-chloroanisole and first order in salt according to the rate equation

$$-\frac{d(\text{Cl}_2)}{dt} = k_c(\text{ArH})(\text{Cl}_2)(\text{Salt}) \quad (19)$$

where (salt) refers to the concentration of the various salts used.

The results are shown in Table VII and a typical plot of  $-\log A$  versus time for each salt is shown in Figure VI and Figure VII.

The values of the rate constants,  $k_c$ , obtained for each salt along with the standard deviation are therefore

Pyridine Hydrochloride	$k_c = 7.9 \pm 0.3 \times 10^{-2} \text{ lt.}^2 \text{ mole}^{-2} \text{ sec.}^{-1} .$
N-ethylpiperidine Hydrochloride	$k_c = 2.66 \pm 0.02 \times 10^{-2} \text{ lt.}^2 \text{ mole}^{-2} \text{ sec.}^{-1} .$
Tetrabutylammonium Perchlorate	$k_c = 11.1 \pm 0.6 \times 10^{-2} \text{ lt.}^2 \text{ mole}^{-2} \text{ sec.}^{-1} .$
Tetrabutylammonium Chloride	Not Constant

TABLE VII

THIRD ORDER RATE CONSTANTS,  $k_c$ , FOR THE CHLORINATION OF  
 P-CHLOROANISOLE IN CHLOROFORM IN THE PRESENCE  
 OF ADDED SALTS.  
 $t=25^\circ\text{C}$

(ArH) (Mole/lit.)	(Cl <sub>2</sub> ) × 10 <sup>2</sup> (mole/lit.)	(salt) × 10 <sup>2</sup> (Mole/lit.)	$k_c \times 10^2$ (Lt <sup>2</sup> .m. <sup>2</sup> sec. <sup>-1</sup> )	Salt
0.272	1.35	1.15	7.8	Pyridine Hydrochloride
0.544	0.675	2.30	8.3	
0.271 <sup>(1)</sup>	1.78	2.63	8.5	
0.541	0.898	5.26	7.3	
0.218	0.672	1.28	10.3	Tetrabutyl- ammonium Perchlorate
0.218	0.672	2.70	12.3	
0.436 <sup>(2)</sup>	0.336	2.56	11.3	
0.436	0.336	4.60	10.8	
0.650 <sup>(3)</sup>	0.178	5.74	2.68	N-Ethyl- piperidine Hydrochloride
0.325	0.356	2.87	2.63	
0.325	0.356	3.42	2.66	
0.813	0.453	9.27	11.1	Tetrabutyl- ammonium Chloride
0.407	0.906	4.64	21.0	
0.325	0.453	3.70	23.6	
0.163 <sup>(4)</sup>	0.906	1.85	34.5	
0.163	0.453	1.85	32.6	

(1) and (2) are plotted on Figure VI

(3) and (4) are plotted on Figure VII

FIG VI Plots of  $-\text{Log } A$  versus Time for the chlorination of p-chloroanisole in chloroform in the presence of added salts.

(1) Chlorine  $1.78 \times 10^{-2}$  M.

p-Chloroanisole 0.271 M.

Pyridine Hydrochloride  $2.63 \times 10^{-2}$  M.

(2) Chlorine  $0.336 \times 10^{-2}$  M.

p-Chloroanisole 0.436 M.

Tetrabutylammonium Perchlorate

$2.56 \times 10^{-2}$  M.

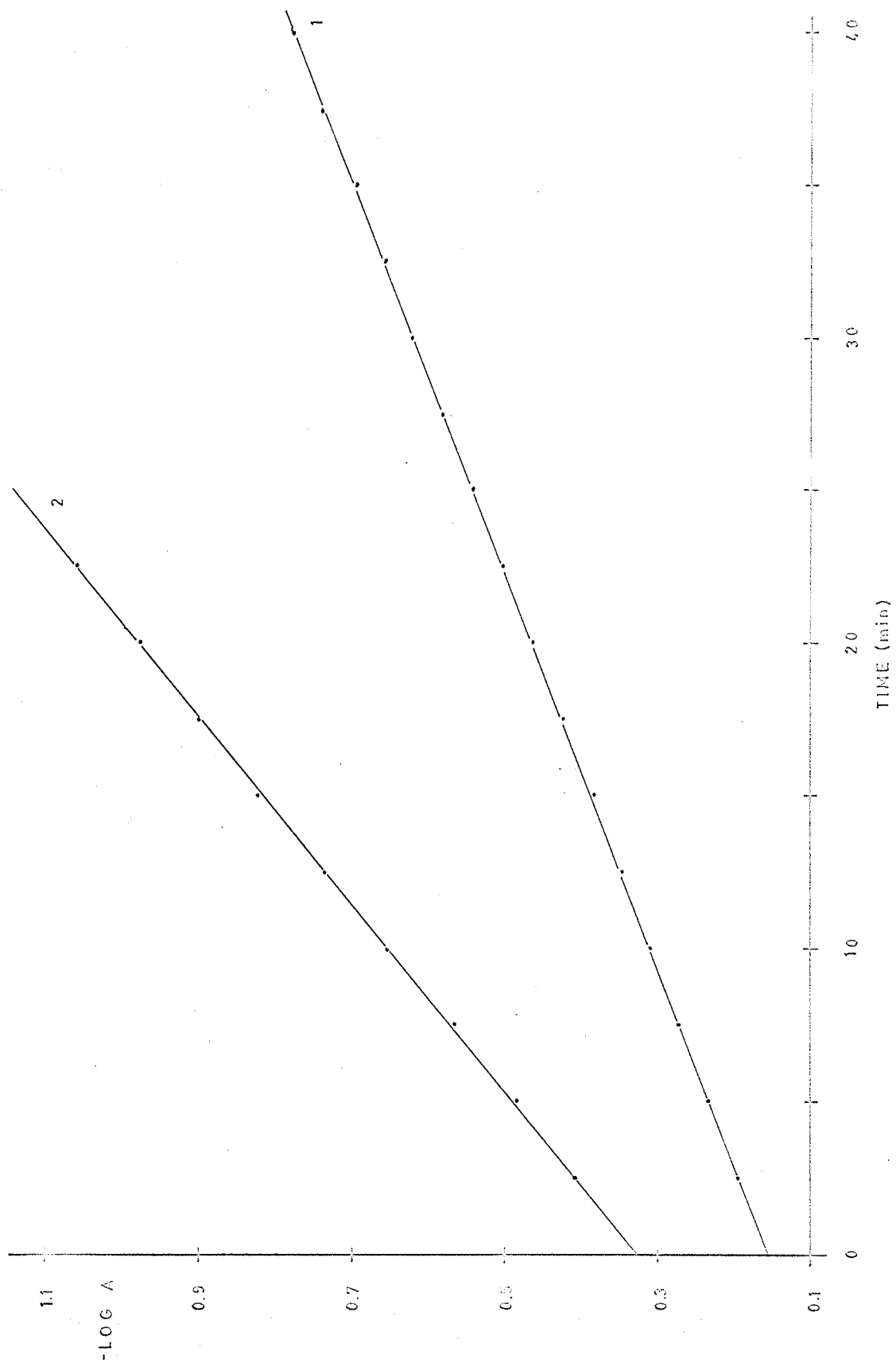


FIG. VI

FIG VII Plots of  $-\text{Log } A$  versus Time for the chlorination of p-chloroanisole in chloroform in the presence of added salts.

(3) Chlorine  $0.178 \times 10^{-2} \text{ M.}$

p-Chloroanisole  $0.650 \text{ M.}$

N-Ethylpiperidine Hydrochloride

$5.74 \times 10^{-2} \text{ M.}$

(4) Chlorine  $0.906 \times 10^{-2} \text{ M.}$

p-Chloroanisole  $0.163 \text{ M.}$

Tetrabutylammonium Chloride

$1.85 \times 10^{-2} \text{ M.}$

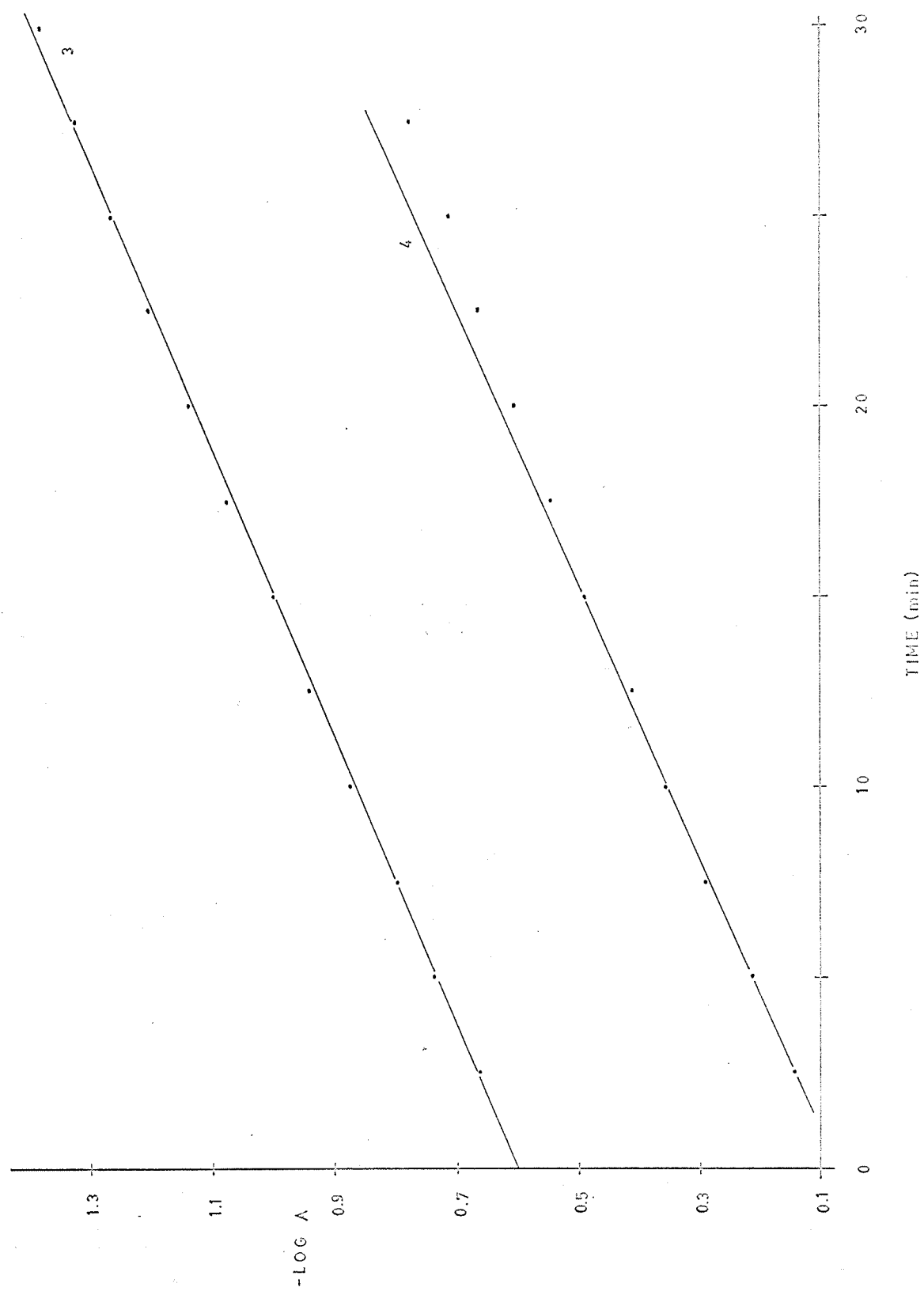


FIG. VII



4. Chloroform with Pyridine: A few rate measurements were made of the chlorination of p-chloroanisole in chloroform in the presence of pyridine. In all cases the pyridine concentration was much larger than the initial chlorine concentration so that pyridine consumed by HCl liberated in the reaction could be ignored.

The plots of  $-\log A$  versus time are shown for three runs on Figure VIII. The plots curve quite rapidly from the expected first order relationship of equation 8. An attempt was made to evaluate the initial rate constants,  $k_A$  by the initial slope procedure described earlier ( page 39). The results are shown in Table VIII.

TABLE VIII  
CHLORINATION OF P-CHLOROANISOLE IN  
CHLOROFORM WITH PYRIDINE  
 $t=25^\circ\text{C}$

(ArH) Moles/lit.	(Cl <sub>2</sub> ) × 10 <sup>3</sup> Moles/lit.	(Pyridine) × 10 <sup>2</sup> Moles/lit.	$k_A \times 10^4$ Lt. mole <sup>-1</sup> sec. <sup>-1</sup>
0.326	6.72	8.11	4.85
0.326	6.72	9.95	4.51
0.326	6.72	15.4	4.06

FIG. VIII Plots of  $-\text{Log } A$  versus Time for the chlorination of p-chloroanisole in chloroform in the presence of pyridine. This is the experimental data of the runs from Table VIII.

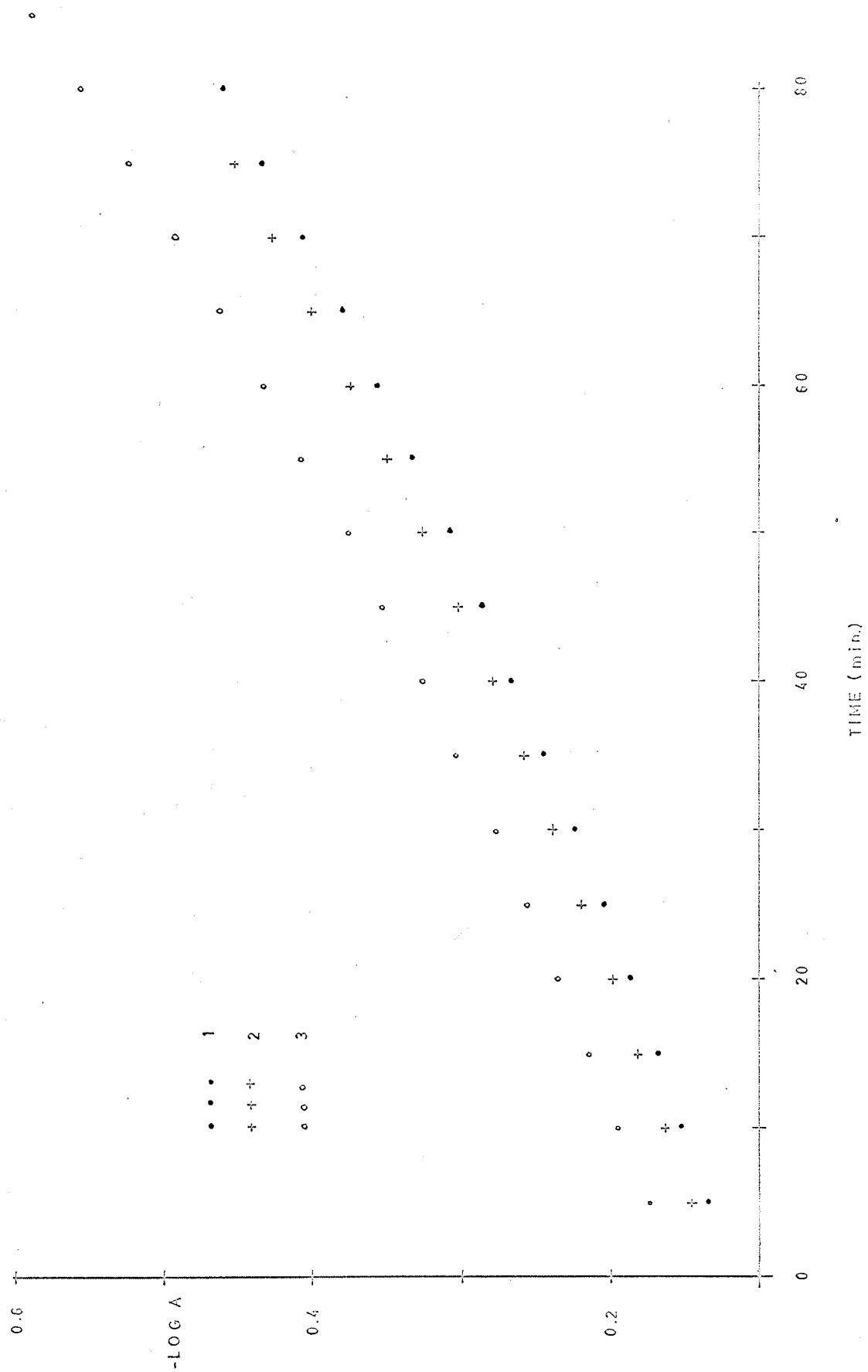


FIG. VIII

## B CHLORINATION OF TOLUENE IN ACETIC ACID

The chlorination of toluene in acetic acid was found to obey the simple second order rate equation

$$-\frac{d(\text{Cl}_2)}{dt} = k_2(\text{ArH})(\text{Cl}_2) \quad (20)$$

where

$(\text{ArH})$  is the toluene concentration in moles  $\text{lt.}^{-1}$

$(\text{Cl}_2)$  is the chlorine concentration in moles  $\text{lt.}^{-1}$

$k_2$  is the second order rate constant in  $\text{lt.}^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$ .

Since the reactions were followed by iodine - thiosulphate volumetric methods the chlorine concentration had to be larger than in the spectrophotometric studies and therefore the simplified "pseudo" first order rate expression could not be used. The following method was used to evaluate  $k_2$ .

Let  $(\text{Cl}_2) = a - x$  where  $a$  is the initial chlorine concentration and  $x$  is the amount of chlorine reacted.

Let  $(\text{ArH}) = b - x$  where  $b$  is the initial toluene concentration and  $x$  is the amount reacted.

The rate equation 20 now becomes

$$-\frac{d(\text{Cl}_2)}{dt} = \frac{dx}{dt} = k_2(a-x)(b-x) \quad (21)$$

Equation 21 can easily be integrated

$$\frac{1}{a-b} \ln \frac{a-x}{b-x} = k_2 t + I \quad (22)$$

By applying the initial conditions that  $x = 0$  when  $t = 0$  the integration constant  $I$  can be evaluated

$$I = \frac{1}{a-b} \ln \frac{a}{b} \quad (23)$$

Substituting equation 23 in equation 22 and rearranging gives

$$\ln \frac{a-x}{b-x} = (a-b)k_2 t + \ln \frac{a}{b} \quad (24)$$

Converting equation 23 to base 10 logarithms

$$\log \frac{a-x}{b-x} = \frac{a-b}{2.3} k_2 t + \log \frac{a}{b} \quad (25)$$

By plotting  $\log \frac{a-x}{b-x}$  versus time a straight line of slope  $m = \frac{a-b}{2.3} K$  and intercept  $\log \frac{a}{b}$  should be obtained.

A typical example of the data is shown in Table IX and the data are plotted on Figure IX. The rate constant for this run evaluated from the slope is  $k_2 = 5.20 \times 10^{-4} \text{ lt.}^2 \text{ mole}^{-2} \text{ sec}^{-1}$ .

TABLE IX

CHLORINATION OF TOLUENE IN ACETIC ACID.  
PLOTTED IN FIGURE XI

Time (min.)	$(\text{Cl}_2) \times 10^2$ a-x Moles/lit.	(ArH) b-x Moles/lit.	Log $\frac{a-x}{b-x}$
0.0	4.24	0.1265	0.4747
55.0	3.43	0.1184	0.5376
83.1	3.11	0.1152	0.5686
128.0	2.66	0.1107	0.6198
165.0	2.32	0.1073	0.6654
242.0	1.83	0.1024	0.7471

The chlorinations in acetic acid were tried with several salts: pyridinium nitrate, lithium chloride; as well as with pyridine itself. In all cases good second order rate constants were obtained. The results are shown in Table X along with some literature values.

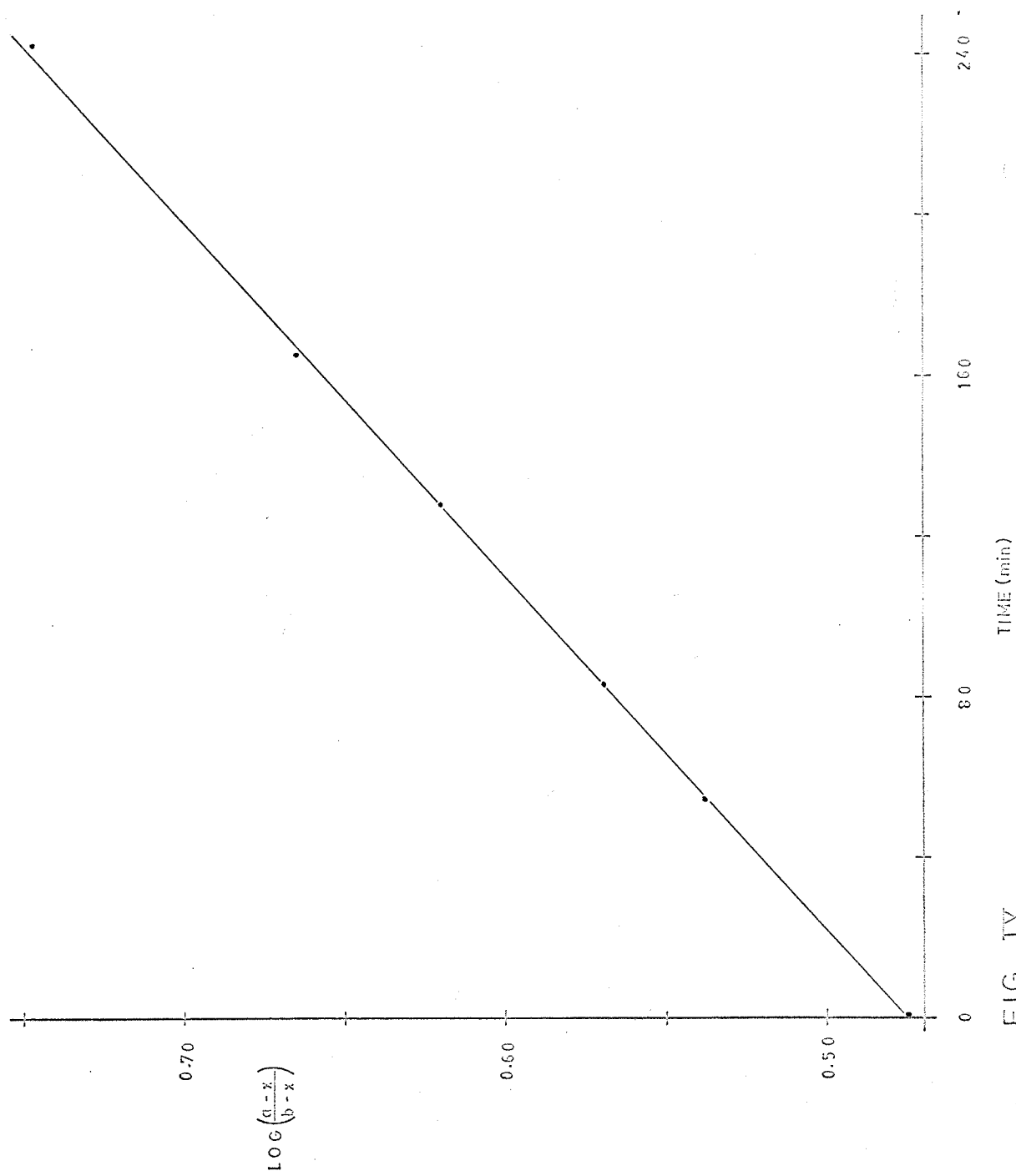


FIG. IX

TABLE X  
 SECOND ORDER RATE CONSTANTS FOR THE CHLORINATION OF  
 TOLUENE IN ACETIC ACID.  
 t=25°C

$(\text{Cl}_2) \times 10^2$ Moles/lit.	(ArH) Moles/lit.	(Salt) Moles/lit.	$k_2 \times 10^4$ Lt. m. <sup>-1</sup> sec. <sup>-1</sup>
4.24	0.1265		5.05
2.58	0.1697		4.65
6.44	0.2351		4.95
6.31	0.2326		4.96
6.16	0.3774		4.46
5.96	0.3540	Pyridinium Nitrate: 0.0313	6.36
8.99	0.3746		4.55
9.14	0.3710	Lithium Chloride 0.0313	5.45
9.71	0.3912		4.66
9.34	0.3894	Pyridine: 0.0228	5.62

The literature values for the chlorination of toluene in acetic acid are listed below for comparison.

$(\text{Cl}_2) \times 10^2$ Moles/lit.	(ArH) Moles/lit.	$k_2 \times 10^4$ Lt. m. <sup>-1</sup> sec. <sup>-1</sup> and reference
2.5	0.10	5.0 (20)
2.7-0.7	0.4-0.1	6.5 (36)
3.1-3.4	0.19	5.3 (13)
9.3	0.16	5.3 (22)
14.2	0.83	3.8 (22)



## II EVALUATION OF THE TRICHLORIDE ION FORMATION CONSTANT IN THE SYSTEM TETRABUTYLAMMONIUM CHLORIDE AND CHLORINE IN CHLOROFORM

### PRELIMINARY DATA:

Solutions of various concentrations of tetrabutylammonium chloride and chlorine in chloroform were scanned on the spectrophotometer over the range  $400\text{m}\mu$  to  $250\text{m}\mu$ . The spectrum in Figure X has the chlorine concentration in large excess of the salt concentration whereas in Figure XI the salt concentration is in large excess of the chlorine concentration. In both cases the absorbance due to the tetrabutylammonium chloride and in Figure XI the absorbance due to chlorine is negligible ( $<0.01$ ) for this type of qualitative work. Also in both cases the actual absorbance,  $A$  (referred to 1.0 cm. cells), is plotted against wavelength.

For comparison with another salt a spectrum of tetrabutylammonium perchlorate and chlorine in chloroform is shown in Figure XII along with a spectrum of chlorine at the same concentration.

### B BENESI-HILDEBRANDE EVALUATION OF TRICHLORIDE ION FORMATION CONSTANT

As discussed previously (Page 15) in the literature Section, Part II a modified form of the Benesi-Hildebrand equation was used to evaluate the equilibrium constant  $K$

FIG. X A spectrum of Tetrabutylammonium Chloride ( $8.15 \times 10^{-4}$  M.) and Chlorine ( $2.47 \times 10^{-2}$  M.) along with a spectrum of Chlorine at the same concentration ( $2.47 \times 10^{-2}$  M.) for comparison.

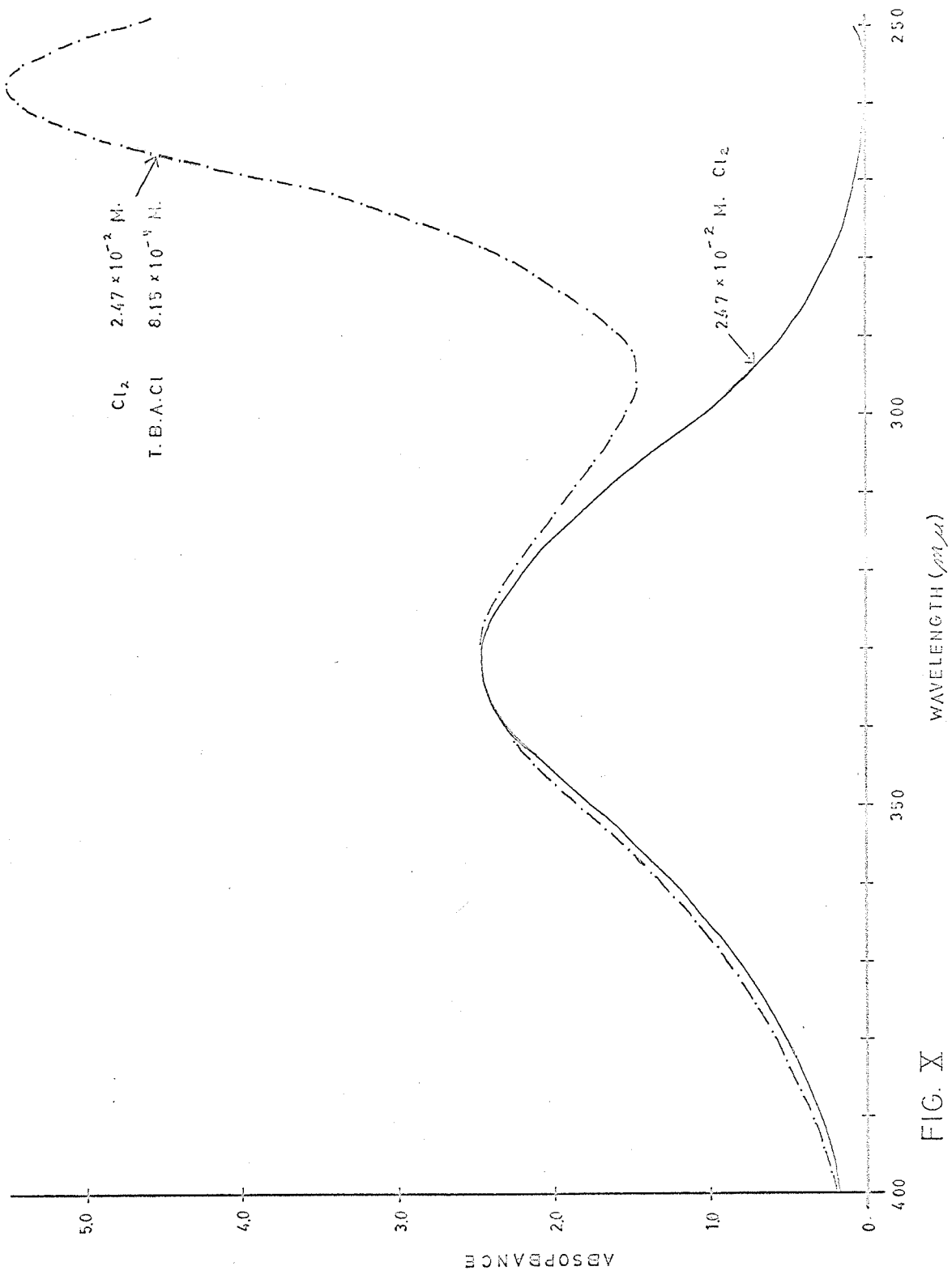


FIG. X

FIG. XI A spectrum of Tetrbutylammonium Chloride ( $3.65 \times 10^{-3}$  M.)  
and Chlorine ( $1.36 \times 10^{-4}$  M.)

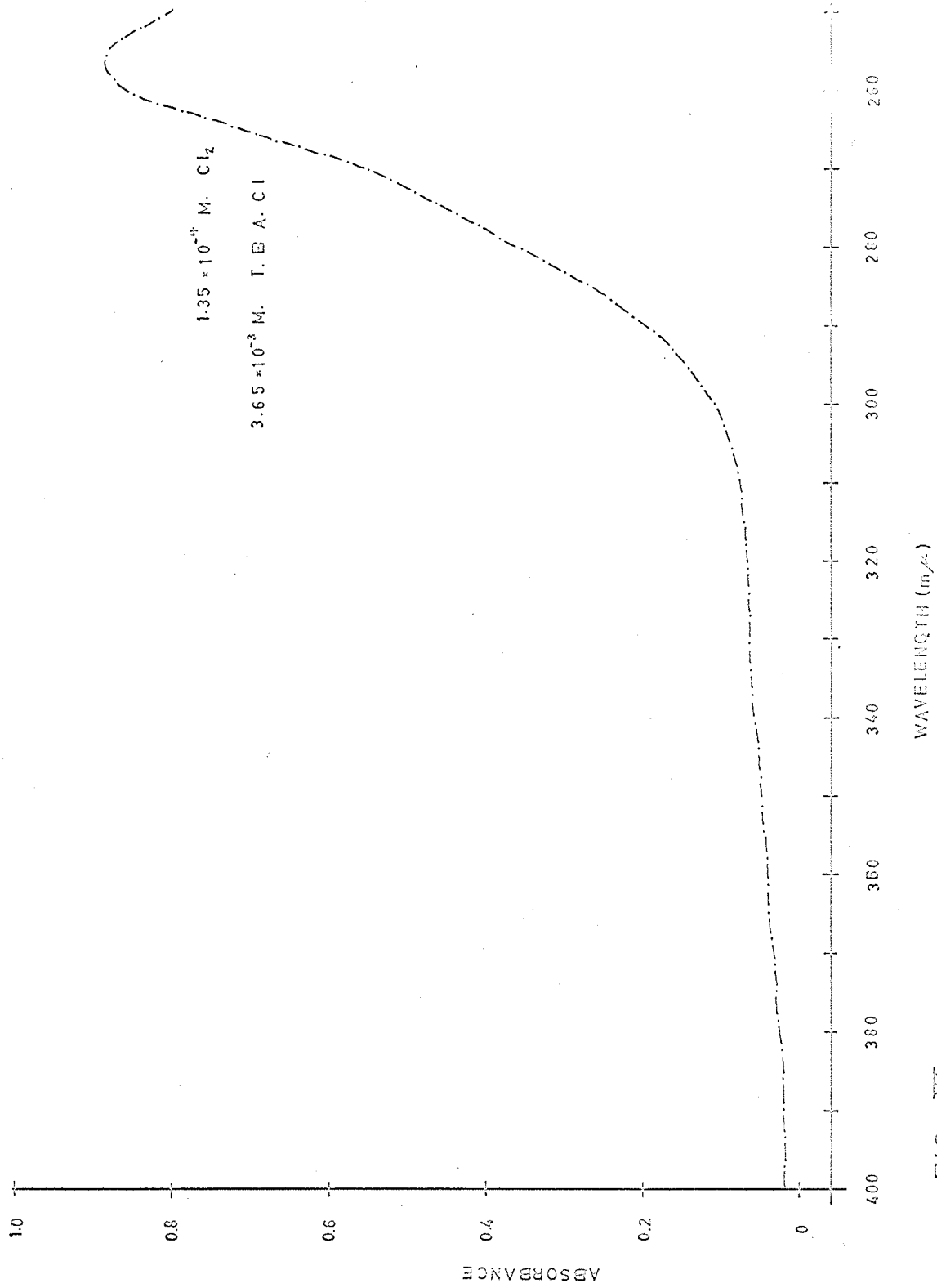


FIG XI

FIG. XII A spectrum of Tetrabutylammonium Perchlorate  
( $9.35 \times 10^{-2}$  M.) and Chlorine ( $1.26 \times 10^{-2}$  M.)  
along with a spectrum of Chlorine ( $1.26 \times 10^{-2}$  M.)  
for comparison.

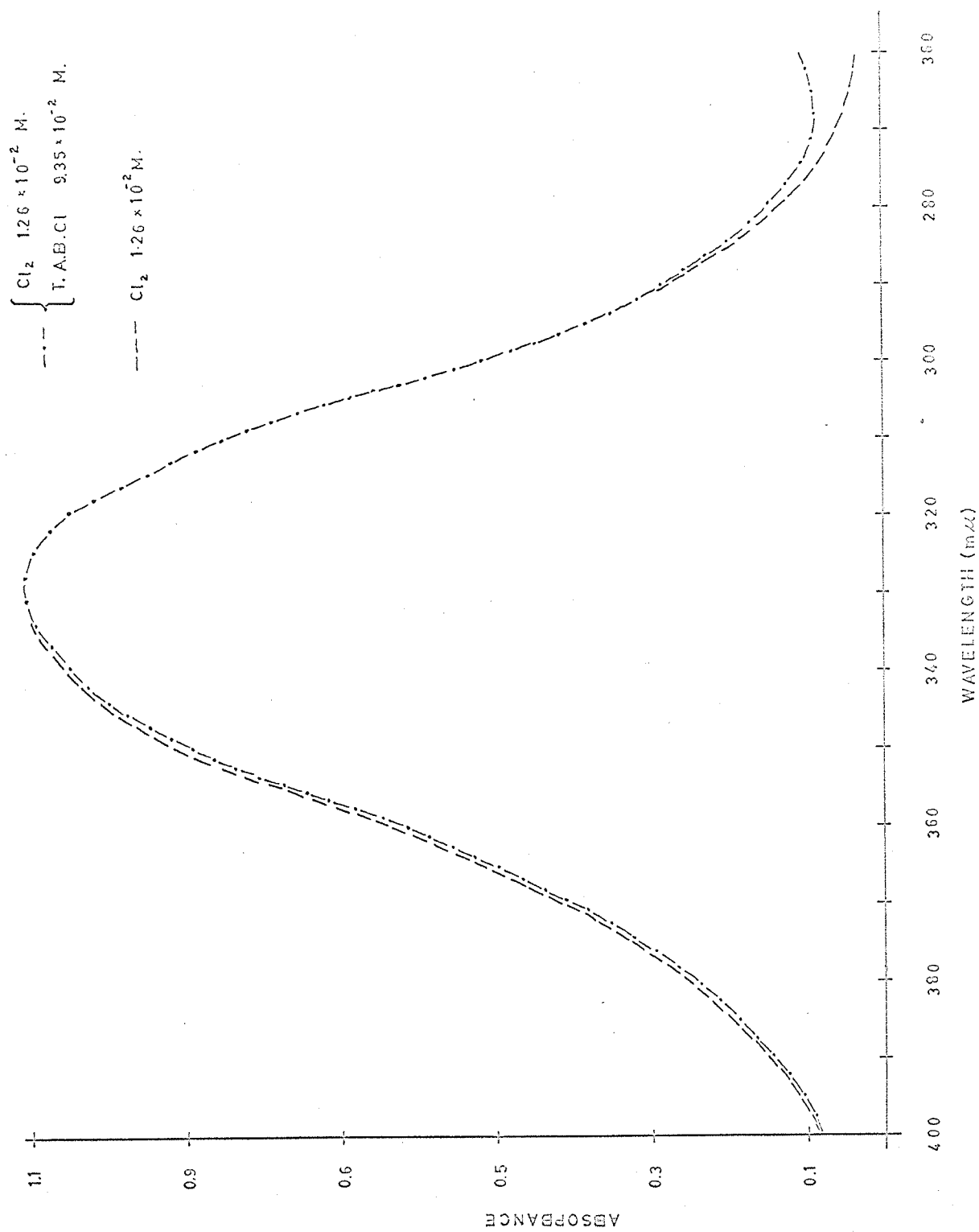
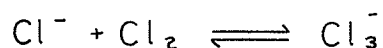


FIG. XII

for the process



where

$$K = \frac{(\text{Cl}_3^-)}{(\text{Cl}^-)(\text{Cl}_2)}$$

The equation used was

$$C_b^0 = \frac{\epsilon C_A^0 C_b^0}{D} - \frac{1}{K}$$

where  $C_A^0$  is the initial chlorine concentration

$C_b^0$  is the initial tetrabutylammonium chloride concentration.

$D$  is the absorbance of the solution minus the contribution to the absorbance by the chlorine and the salt at concentrations  $C_A^0$  and  $C_b^0$  respectively. Therefore a plot of  $\frac{C_A^0 C_b^0}{D}$  versus  $C_b^0$  should give a straight line of slope  $\epsilon$  and intercept  $-\frac{1}{K}$ .

The results obtained at  $305_{m\mu}$  and  $t = 25.0^\circ\text{C}$  are shown in Table XI and plotted in Figure XIII. The terms  $C_A^0$ ,  $C_b^0$ , and  $D$  have been defined and  $A$  represents the actual measured value of the absorbance.

Some discussion of the experimental error in the values obtained is necessary. As mentioned in the Experimental Section, Part II (Page 32) a solution of chlorine and tetrabutylammonium chloride in chloroform is not stable with time and hence the values of the absorbance



TABLE XI

DATA FOR THE BENESI-HILDEBRAND EVALUATION OF THE TRICHLORIDE ION  
FORMATION CONSTANT, K, IN THE SYSTEM TETRABUTYLAMMONIUM  
CHLORIDE IN CHLOROFORM.

$t=25^{\circ}\text{C}$

$\lambda=305\text{ m}\mu$ .

$C_B \times 10^2$ Moles/lit.	$C_A \times 10^4$ Moles/lit.	A	D	$\frac{C_B C_A}{D} \times 10^5$ Moles <sup>2</sup> lit. <sup>-2</sup>
3.24	4.54	0.305	0.278	5.29
4.75	4.66	0.412	0.372	5.95
6.19	4.98	0.578	0.534	5.77
7.27	4.56	0.544	0.498	6.68
8.35	4.66	0.564	0.514	7.54
10.1	4.07	0.551	0.503	8.15
10.4	4.87	0.693	0.637	7.97
13.0	4.67	0.639	0.579	10.4
16.8	4.49	0.734	0.664	11.7

FIG. XIII A plot of the experimental data in Table XI for the Benesi-Hildebrand evaluation of the trichloride ion formation constant,  $K$ .

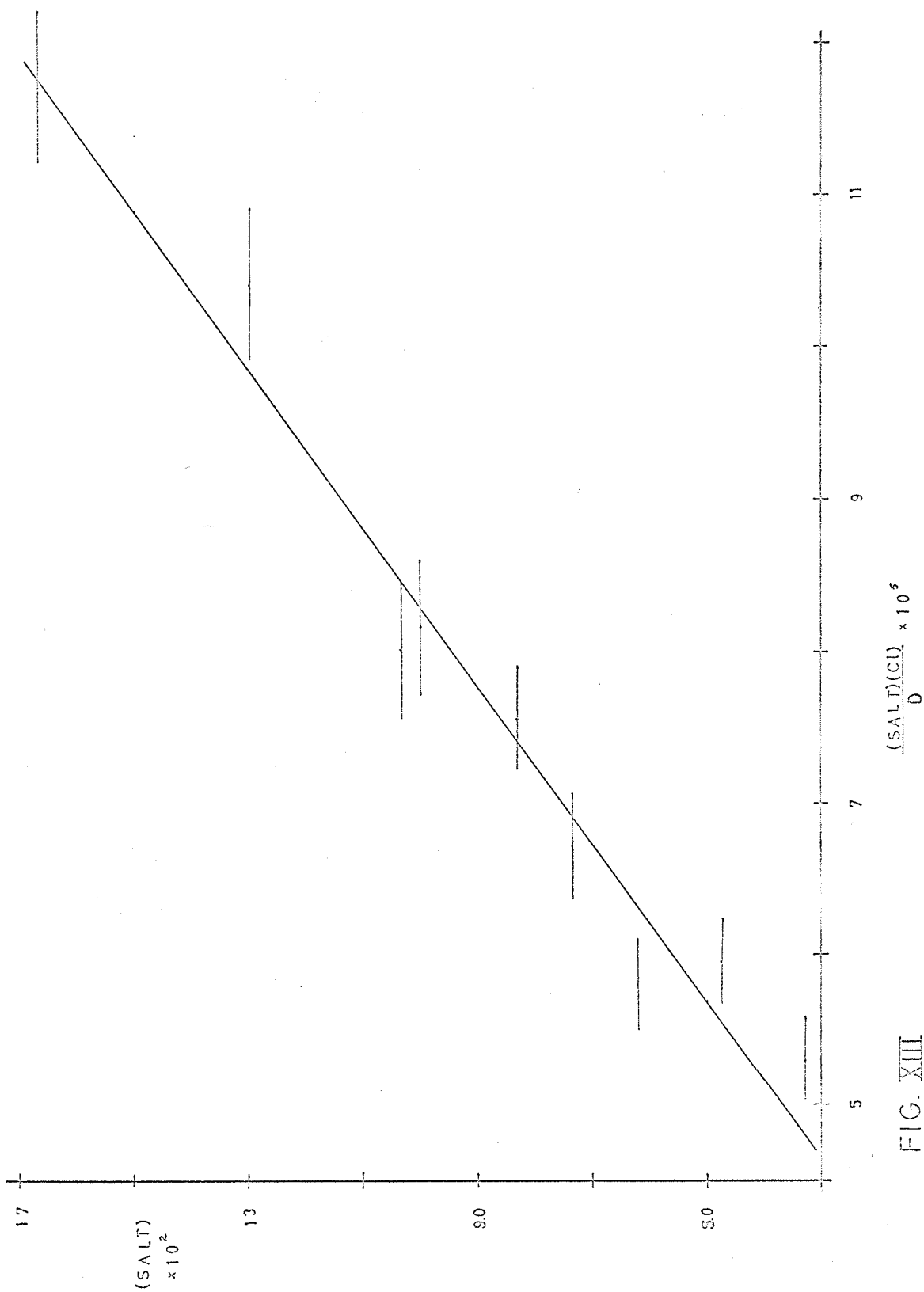


FIG. XIII

were obtained by extrapolating a series of values back to zero time. Consequently the error in this quantity is larger than would normally be expected for a spectrophotometric measurement. The estimated error in the quantity  $A$  is therefore about  $\pm 3\%$  and the error in the quantity  $\frac{C_0 C_A}{D}$  is estimated at  $\pm 5\%$  due to other errors in the experimental method. These errors are shown on the graph in Figure XIII. Very little error is associated with the value  $C_0$ .

Although there is quite a scatter in the experimental points from the expected straight line there are no trends towards curvature in any one direction. A least squares treatment of the data gives the straight line shown in Figure XIII. The value of the equilibrium constant, obtained from the intercept, and the absorptivity, equal to the slope, along with their standard deviations are

$$K = 17 \pm 3 \text{ lt. mole}^{-1}$$

and  $\epsilon = 1900 \pm 140 \text{ lt. mole}^{-1} \text{ cm}^{-1}$

#### C OTHER ATTEMPTS TO EVALUATE TRICHLORIDE ION FORMATION CONSTANT

Some attempts were made to verify the value of  $K = 17 \pm 3 \text{ lt. mole}^{-1}$  obtained in the previous section.

The obvious method is to reverse the concentration conditions and do the measurements with chlorine in large excess of the tetrabutylammonium chloride concentration.

However it was found impossible to work at high enough chlorine concentrations to satisfy the conditions of greater than 10% of the low concentration component (i.e. the salt) complexed (53). These attempts were therefore abandoned. Actually this method would have been preferable to the method used in Section B as the solutions with low salt concentration are stable with time and give constant absorbance values.

An attempt was made to work at approximately equal concentrations of salt and chlorine and use the Rose-Drago method (56) for the evaluation of  $K$ . However this method also failed because insufficient percentage of the low concentration component was complexed. It is of interest to note, however, that an approximate value of 10 lt. mole<sup>-1</sup> for  $K$  was obtained with chlorine concentration equal to  $2.9 \times 10^{-2}M$ . and salt concentration from  $7.0 \times 10^{-2}M$ . to  $15 \times 10^{-2}M$ .

There seemed little point working at conditions similar to those used in Section B but at slightly different wavelengths. To work at very different wavelength ( for instance around the maximum absorbance of complex at  $255m\mu$ ) would require using small cuvettes (1 mm.). Since with high salt concentrations it was necessary to mix the solutions right in the cuvette to obtain accurate values of absorbance, the use of the small cuvettes seems unfeasible.

## DISCUSSION

From the brief study of Cohen's work (Experimental, Section C) it appears that pyridine does have some catalytic activity in the chlorination of benzene. However, there is a discrepancy in the results of the two methods as chlorobenzene was formed only in the second method.

In the first method, where chlorine was passed continuously through the reaction mixture, the only chlorination product obtained was the addition compound, benzenehexachloride. Note that this must also be the method used by Cohen in order to account for the high yields of chlorobenzene. Presumably a mixture of the various isomers of benzenehexachloride was actually produced but the purification gave only the  $\alpha$ -isomer. The fact  $\alpha$ -benzenehexachloride was formed is not surprising since this is one of the standard methods of preparation (30,46). However there seems to be no good explanation for the lack of chlorobenzene in this work or for the lack of benzenehexachlorides in Cohen's work. Since Cohen gives no details as to purification of chemical perhaps some impurities in the benzene or chlorine prevented the occurrence of the free radical addition reaction. Conversely the purification of the benzene and chlorine for this work may have made the free radical reaction go at a fast enough rate so that simultaneous formation of chlorobenzene by an ionic substitution mechanism would not occur.

In the second method used in this work the reaction

flask was screened from the light in an attempt to prevent the free radical addition reaction. The results (Table I) indicate that pyridine does have some catalytic activity. In the absence of pyridine the reaction was extremely slow (less than 0.5% chlorobenzene after 19 hours) but in the presence of pyridine, the reaction was complete in only 6 hours. Note also that the yields are quite good since a saturated solution of chlorine at room temperature predicts 12% chlorobenzene and the actual yield is 9 - 10%. Presumably the yields at 60°C (the reaction temperature) would be less because of volatility losses of chlorine.

Some discussion of the possible mechanism for pyridine acting as a catalyst in this type of system will now be given. As mentioned in the Review of the Literature, Section IB, the usual catalysts act by polarizing the chlorine-chlorine bond and therefore creating a more electrophilic reagent. The original explanation for the activity of pyridine was essentially the same (16). Pyridine, a so-called "halogen-carrier" was visualized as forming some type of pyridine-chlorine compound that made the chlorine a more reactive agent. The other possibility for the activity of pyridine would be a salt or medium effect. In other words pyridine or pyridine hydrochloride should increase the polarity of the medium and make the reaction proceed faster. However at the very low

concentrations of pyridine used it is surprising that such a large medium effect would occur even when the sensitivity of aromatic chlorination to solvent effects is considered.

At this point it should be noticed that the discussion of the catalytic activity of pyridine assumes both pyridine and pyridine hydrochloride would be effective. This seems reasonable in view of the very low concentrations of pyridine used in Cohen's method. The pyridine would be converted to pyridine hydrochloride after a very low percent reaction and hence, if only pyridine was a catalyst, the reaction would again become extremely slow.

During the attempts to repeat Cohen's chlorination with pyridine in benzene, pyridine hydrochloride precipitated from the reaction system. This fact makes interpretation of the data very difficult since the activity of the catalyst in the two phase system is unpredictable. Also, once the pyridine hydrochloride has precipitated the actual concentration of pyridine or its salt in solution should be extremely low. In view of these difficulties a solvent system was adopted in order to obtain more quantitative results.

The actual system used in the work was p-chloroanisole in chloroform. Chloroform was chosen because it is a relatively non-polar solvent;  $\epsilon = 4.8$  at  $20^{\circ}\text{C}$  (43); corresponding to Cohen's conditions of pure benzene, and yet will dissolve pyridine hydrochloride and the other salts



used in this work. *p*-Chloroanisole was selected as an aromatic substrate because it reacts at a convenient rate for kinetic studies and because only one product 2,4-dichloroanisole is obtained (Experimental, Section E).

Initially the chlorination of *p*-chloroanisole was studied in the absence of any catalyst so that some results for comparison would be available. The reaction in chloroform agrees qualitatively with the work of Andrews and Keefer for non-polar solvents although the induction periods and erratic kinetics reported for the chlorination of pentamethylbenzene in carbon tetrachloride (37) and toluene in ethylene chloride (3) were not observed. The reactions were autocatalytic however, presumably due to the HCl produced as one of the products of the reaction (Figure II). In order to test the hypothesis that the autocatalytic behaviour was due to HCl, rate runs were carried out with excess HCl which were found to obey the kinetic expression

$$-\frac{d(\text{Cl}_2)}{dt} = k_B(\text{ArH})(\text{Cl}_2)(\text{HCl}) \quad (1)$$

where  $k_B = 1.43 \times 10^{-2} \text{ l}^2 \text{ mole}^{-2} \text{ sec}^{-1}$  (Table V). Further proof for the first order in HCl term was obtained by applying a combined rate expression of the form

$$-\frac{d(\text{Cl}_2)}{dt} = (\text{ArH}) [k_A + k_B(\text{HCl})] (\text{Cl}_2) \quad (2)$$

for the cases where HCl is not in excess. Using the known values of  $k_A = 1.01 \times 10^{-4} \text{ lt.mole}^{-1} \text{ sec.}^{-1}$  and  $k_B = 1.43 \times 10^{-2} \text{ lt.}^2 \text{ mole}^{-2} \text{ sec.}^{-1}$  the experimental data was found to fit equation 2 very well (Figure V).

The fact that the reactions are first order in HCl has been observed for several cases of aromatic chlorination in non-polar solvents (3, 57). However, Andrews and Keefer (37) report a more complicated order for the chlorination of pentamethylbenzene in carbon tetrachloride.

$$-\frac{d(\text{Cl}_2)}{dt} = 8.9 \times 10^{-3} (\text{ArH})(\text{Cl}_2)(\text{HCl})^{3/2} \quad (3)$$

Or

$$-\frac{d(\text{Cl}_2)}{dt} = [0.62(\text{HCl}) + 26.9(\text{HCl})^2](\text{ArH})(\text{Cl}_2) \quad (4)$$

In view of the extremely large percent side chain chlorination observed in their system (at a ratio of two moles of chlorine to one mole of aromatic, virtually all the pentamethylbenzene was converted to a dichloro derivative of pentamethylbenzene) some doubt should be placed on the reliability of their measurements.

Rate data were also obtained for the chlorination of p-chloroanisole in chloroform in the presence of added reagents such as pyridine, pyridine hydrochloride, N-ethylpiperidine hydrochloride, tetrabutylammonium chloride and

tetrabutylammonium perchlorate. A summary of the results is given in Table XII. The  $k_2$  refers to second order rate constants obtained by the initial slope method. (Results, Section I A).

$$-\frac{d(\text{Cl}_2)}{dt} = k_2(\text{ArH})(\text{Cl}_2)$$

and the  $k_3$  refers to third order rate constants

$$-\frac{d(\text{Cl}_2)}{dt} = k_3(\text{ArH})(\text{Cl}_2)(\text{Salt})$$

Since ionic strength is so important in the chlorination of aromatic compounds in non-polar solvents the third order rate constants in Table XII will all be converted to second order rate constants at a fixed salt concentration so that a comparison can be made between the kinetics for these salts and those with pyridine and pure chloroform. In other words, although HCl, tetrabutylammonium perchlorate, N-ethylpiperidine hydrochloride, and pyridine hydrochloride obey the relationship

$$-\frac{d(\text{Cl}_2)}{dt} = k_3(\text{ArH})(\text{Cl}_2)(\text{Salt})$$

at a constant salt concentration (say,  $9.5 \times 10^{-2}$  M.) they will obey the pseudo second order relationship

$$-\frac{d(\text{Cl}_2)}{dt} = k_2'(\text{ArH})(\text{Cl}_2)$$

where  $k_2' = k_3(\text{salt})$ . Also a value of  $k_2'$  is available for tetrabutylammonium chloride at  $9.3 \times 10^{-2}$  M. in salt

TABLE XII

SUMMARY OF RATE CONSTANTS FOR THE CHLORINATION  
OF P-CHLOROANISOLE IN CHLOROFORM.  
 $t=25^{\circ}\text{C}$

Added Reagent	$k_2 \times 10^4$ Lt. mole <sup>-1</sup> sec <sup>-1</sup>	$k_3 \times 10^2$ Lt. <sup>2</sup> mole <sup>-2</sup> sec <sup>-1</sup>
Pure chloroform	1.01	-
Pyridine	Not Constant	-
HCl	-	1.43
N-Ethylpiperidine HCl	-	2.66
Pyridine HCl	-	7.9
T.B.A. ClO <sub>4</sub> <sup>(1)</sup>	-	11.1
T.B.A. Cl <sup>(1)</sup>	-	Not Constant

TABLE XIII

COMPARISON OF RATE CONSTANTS FOR THE CHLORINATION  
OF P-CHLOROANISOLE IN CHLOROFORM WITH ADDED REAGENTS.

Added Reagent	Concentration (Moles/lit.) $\times 10^2$	$k_2$ or $k_2' \times 10^4$ Lt. mole <sup>-1</sup> sec <sup>-1</sup>
Pure chloroform	-	1.01
Pyridine	9.9	4.51
HCl	9.5	13.6
N-Ethylpiperidine HCl	9.5	24.6
Pyridine HCl	9.5	75.0
T.B.A. ClO <sub>4</sub> <sup>(1)</sup>	9.5	103
T.B.A. Cl <sup>(1)</sup>	9.3	103

(1) T.B.A. refers to the tetrabutylammonium ion.

and a value of  $k_2$  for pyridine at  $9.9 \times 10^{-2}$  M. in pyridine so that all catalysts can be compared at a similar concentration. The results of this comparison are shown in Table XIII.

From the data in Table XIII, it would appear that neither pyridine or pyridine hydrochloride has any special catalytic activity. The other salts are just as effective in increasing the rate of the reaction over that in pure chloroform and in fact are better in some cases. The interesting fact is that the order of reactivity is in the same order as the predicted polarity of the salts in chloroform. Tetrabutylammonium chloride and tetrabutylammonium perchlorate should be the most polar since they can exist only as ions, or ion pairs in the chloroform solvent. The other three salts HCl, pyridine hydrochloride and N-ethylpiperidine hydrochloride should have some covalent character in the non-ionizing solvent and hence would be less polar. Pyridine itself, which has a dielectric constant of 12.3 at 25 ° C (75), would be expected to be the least effective in increasing the polarity of the medium. Therefore the most reasonable explanation for the catalytic activity of the various reagents would be a simple medium effect; the increased polarity of the solvent makes the rate determining conversion of the  $\pi$ -complex to the  $\sigma$ -complex proceed at a faster rate.

If the explanation for the activity of the various salts is a medium effect it is surprising that the rates

appear to be first order (except for tetrabutylammonium chloride) in these salts. Generally the increased polarity of the solvent caused by the presence of the salts would not be expected to follow a first order relationship in salt concentration. However perhaps over the limited range of salt concentrations used ( $1.0 \times 10^{-2}M$  to  $10.0 \times 10^{-2}M$ ) the deviations from linearity would not be apparent. For example Jungers (57) has shown that the chlorination of aromatic compounds is first order in HCl up to 0.4 Molar HCl but then becomes higher than first order. In the present work the low solubility of the salts in chloroform prevented working at higher concentrations.

The other explanation for the first order in salt relationship is that the salt is acting as reagent, E, necessary to polarize the chlorine-chlorine bond in the rate determining step. The reaction would be expected to follow the kinetic relationship

$$-\frac{d(Cl_2)}{dt} = k_3(ArH)(Cl_2)(Salt)$$

However it seems rather difficult to differentiate between a mechanism where the salt increases the polarity of the medium and thus makes the rate determining step proceed faster and a mechanism where the salt polarizes the chlorine-chlorine bond and makes the same rate determining conversion of the  $\pi$ -complex to the  $\sigma$ -complex go faster. These two effects are probably acting simultaneously and can

be regarded as two very similar explanations for the overall effect of a salt on the non-polar medium.

A brief study of the catalytic effect of pyridine and pyridinium nitrate in acetic acid also indicates that these salts have no special activity as catalysts. The increase in rate constants was quite small; the ratio of rate constants for the chlorination of toluene in acetic acid in the presence of 0.03M pyridinium nitrate to that in pure acetic acid is only 1.4 (Table X). The ratio for 0.023M pyridine is only 1.2. This is the same order of magnitude as that for 0.03M LiCl, 1.2, and also the same as that reported for other salts by Robertson (54).

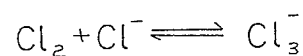
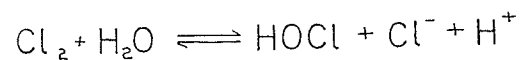
As mentioned previously (Results, Section IA), throughout the course of the kinetic work it was found that various chloride salts had a large effect on the absorbance of chlorine in chloroform. A change in absorbance is not surprising since the absorptivity should be dependent on the nature of the solvent but the extremely large effect of the salts indicated some further interaction. The possibility of trichloride ion formation seemed the most likely explanation so a further study of the system tetrabutylammonium chloride-chlorine in chloroform was attempted. Tetrabutylammonium chloride was chosen in preference to some of the other salts because it is definitely an ionic salt and hence should allow for the strongest interaction between chloride ion and chlorine.

There is some evidence in the literature for the formation of trichloride ion and even measured values of the formation constant. Chattaway (15) has prepared tetraethylammonium trichloride (a yellow, crystalline solid that loses chlorine on standing) by the direct interaction of gaseous chlorine on the salt. However similar procedures with ammonium chloride and alkali metal chlorides failed in agreement with the generalization by Sidgwick (61) that larger cations give stabler perchlorides.

There are several literature values for the trichloride ion formation constant,  $K$ , in water.

$$K = \frac{(\text{Cl}_3^-)}{(\text{Cl}^-)(\text{Cl}_2)}$$

Sherrill and Izard (59) report a value of  $0.01 \text{ lt.mole}^{-1}$  (recalculated by Zimmerman and Strong (73) as  $0.187 \text{ lt.mole}^{-1}$ ) from the solubility of chlorine in aqueous solutions of chloride ion. Zimmerman and Strong (73) obtained a value of  $0.191 \text{ lt.mole}^{-1}$  by a spectrophotometric method in a system involving two equilibria.



The only values reported for non-aqueous solvents are those of Nelson and Iwamoto (45) who used a voltammetric



method. Their values for K are:  $10^{10}$  in acetonitrile; greater than  $10^{12}$  in acetone; greater than  $10^{13}$  in nitromethane. Even more surprising than the extremely large values reported for these formation constants is that they report the order of stability of trihalides as  $\text{Cl}_3^- > \text{Br}_3^- > \text{I}_3^-$  in these solvents which is the reverse of the order in water (61).

In view of the complexity of the systems used to obtain the trichloride ion formation constant in water and, the contrast between the values reported for water and non-aqueous solvents, the simpler system of tetrabutylammonium chloride and chlorine in chloroform should lead to more useful results.

In order to rule out the possibility that the increased values of absorbance observed for the chloride salt were not caused by solvent changes, the spectrum of chlorine with tetrabutylammonium perchlorate was obtained (Figure XII). The very small changes in absorbance indicate that the much larger changes observed for tetrabutylammonium chloride are in fact caused by a charge-transfer complex. However, the fact that the perchlorate salt does have some effect on the absorbance values means that the spectrum of chlorine is altered by the presence of a salt. Therefore, although the change in chlorine absorbance by tetrabutylammonium chloride can be attributed to trichloride ion, some of the change will be due to solvent

effects. This will lead to errors in the experimental points used in the Benesi-Hildebrand treatment which assumes the increased absorbance is caused solely by the formation of a new absorbing species.

The Benesi-Hildebrand evaluation of the formation constant,  $K$ , for the system tetrabutylammonium chloride-chlorine in chloroform gives  $K = 17 \pm 3 \text{ lt.mole}^{-1}$ . A tentative value for the tribromide ion formation constant of  $K \approx 10^5 \text{ lt.mole}^{-1}$  (8) for the system tetrabutylammonium bromide and bromine in chloroform is also available.

These two values are in contrast to the values of Nelson and Iwamoto (45) who have stated  $K$  for trichloride ion should be greater than that for tribromide ion in non-aqueous solvents, but are consistent with the values obtained in water (61). What is more, these values agree with the values predicted by the kinetic results of aromatic chlorination and bromination. The addition of bromide ion to a bromination reaction reduces the rate of reaction tremendously (8, 74), presumably because the tribromide formed is a less active halogenating agent than bromine. If the trichloride ion formation constant was of the order of  $10^{12}$  as Nelson and Iwamoto would predict, the addition of chloride ion should also cut the rate of chlorination reactions tremendously. However, as has been shown (Table VII) the chloride salts increase the

reaction rate in agreement with a much lower value of the formation constant.

It is of interest to note, however, that even with the low value of  $K = 17 \text{ lt.mole}^{-1}$  the addition of tetrabutylammonium chloride will lower the concentration of free chlorine by converting some chlorine to the inactive chlorinating agent, trichloride ion. An expression for the relation between free chlorine and total chlorine can be obtained from equation 14 and equation 15 in the Results, Section IA.

$$(\text{Cl}_2)_F = \left[ \frac{1}{1+K(D)} \right] (\text{Cl}_2)_T \quad (5)$$

where (D) is the tetrabutylammonium chloride concentration. Therefore, assuming trichloride ion is an inactive electrophilic reagent, the actual concentration of chlorinating agent will be less than the total chlorine concentration.

The rate constants discussed previously (Table XII) were obtained from the expression

$$-\frac{d(\text{Cl}_2)}{dt} = k_3(\text{ArH})(\text{Cl}_2)(\text{Salt})$$

where  $(\text{Cl}_2)$  refers to the total chlorine concentration. However as shown by equation 5

$$(\text{Cl}_2)_T = \left[ 1+K(D) \right] (\text{Cl}_2)_F$$

Therefore for the chlorination with tetrabutylammonium chloride the rate expression will be given by

$$-\frac{d(\text{Cl}_2)}{dt} = k_3 [1 + K(D)] (\text{ArH})(D)(\text{Cl}_2)_F$$

and the rate expression in terms of free chlorine, the actual chlorinating agent, is

$$-\frac{d(\text{Cl}_2)}{dt} = k'_3 (\text{ArH})(D)(\text{Cl}_2)_F \quad \text{where } k'_3 = k_3 [1 + K(D)]$$

For the case of tetrabutylammonium chloride ( $9.3 \times 10^{-2} \text{M}$ ) in Table XII and  $K = 17 \text{ lt. mole}^{-1}$ .

$$\begin{aligned} k'_3 &= 11.1 \times 10^{-2} [1 + 17 (9.3 \times 10^{-2})] \\ &= 11.1 \times 10^{-2} \times 2.58 = 28.6 \times 10^{-2} \text{ lt.}^2 \text{ mole}^{-2} \text{ sec.}^{-1} \end{aligned}$$

Converting this to the "pseudo" second order rate constants as in Table XIII gives

$$k'_2 = 228 \times 10^{-4} \text{ lt. mole}^{-1} \text{ sec.}^{-1}$$

However since the value of trichloride ion formation constants are not known for the other chloride salts used in this work, no estimate of the corrected values of  $k_3$  for the other salts can be given. Therefore a full comparison of actual rate constants for chlorination by free chlorine is not possible. However since tetrabutylammonium perchlorate would not be expected to complex

chlorine appreciably the values of  $k_2'$  can be compared for the two tetrabutylammonium salts.

Tetrabutylammonium Chloride  $k_2' = 228 \times 10^{-4} \text{ lt.mole}^{-1} \text{ sec.}^{-1}$   
( $9.3 \times 10^{-2} \text{ M}$ )

Tetrabutylammonium Perchlorate  $k_2' = 103 \times 10^{-4} \text{ lt.mole}^{-1} \text{ sec.}^{-1}$   
( $9.5 \times 10^{-2} \text{ M}$ )

## SUMMARY

1. The results for the chlorination of benzene in pure aromatic as solvent according to Cohen's method (Page 24) are difficult to interpret because undissolved pyridine hydrochloride gives a two phase system. However the indication is that pyridine (or pyridine hydrochloride) has an accelerating effect on the reaction.

2. Rate constants have been obtained for the chlorination of p-chloroanisole in chloroform and for toluene in acetic acid at 25°C. The measurements were made in the pure solvent itself and in the presence of added pyridine, pyridinium salts, and other electrolytes.

3. The results indicate that pyridine and pyridine hydrochloride are not particularly effective as catalysts in aromatic chlorination.

4. The results are best interpreted if the increases in rate are attributed to the increase in polarity of the solvent with the added electrolyte.

5. The trichloride ion formation constant has been obtained for the system tetrabutylammonium chloride - chlorine in chloroform at 25.0°C.

6. The value obtained for the trichloride ion formation constant along with a value for the tribromide ion constant (8) indicate that the order of stability of the trihalides in chloroform is  $\text{Br}_3^- > \text{Cl}_3^-$ .

## SUGGESTIONS FOR FURTHER WORK

1. Since the only indication that pyridine or pyridine hydrochloride might be effective as a catalyst in aromatic chlorination was obtained in the chlorination of benzene by Cohen's method (Page 24) a further study of this type of system might be useful. Recent papers by Olah (47), Lebedev (39,40) and Jungers (19, 41, 42, 51, 57) outline methods for obtaining accurate quantitative data in excess aromatic substrate as solvent. Other electrolytes such as the tetrabutylammonium salts could be used for comparison with pyridine and pyridinium salts.

2. The kinetics of aromatic chlorination in carbon tetrachloride should be attempted in order to check Andrews and Keefer's work (37). Their substrate, penta-methylbenzene, gave extensive side chain chlorination which makes the results seem doubtful. This problem could be avoided by using p-chloroanisole

3. The use of tetrabutylammonium salts could lead to useful information in the measurement of trihalide formation constants. Formation constants could be obtained for  $\text{Cl}_3^-$ ,  $\text{Cl}_2\text{Br}^-$ ,  $\text{ClBr}_2^-$ , and  $\text{Br}_3^-$  by combining bromine and chlorine with the appropriate halide salt. Since these salts are quite soluble in a great variety of solvents it should be possible to find a system that would give excellent results which would be of interest since very few systematic studies of these trihalides in non-polar solvents are available at present.

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