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THE EFFECT OF PYRIDINE
AND PYRIDINIUM SALTS
ON AROMATIC BROMINATION

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ABSTRACT

In order to gain information about the frequently mentioned "pyridine-catalyzed halogenations" the effect of pyridine and pyridinium salts on aromatic bromination has been investigated in both dilute and concentrated solutions of bromine. To aid in interpretation and planning of the experimental work, the effect of other salts on bromination was determined and equilibrium constants were measured for complex formation between pyridinium bromide and bromine and between tetrabutylammonium bromide and bromine in chloroform. Any acceleration in rate caused by pyridine and its salts could be accounted for on the basis of a medium effect or surface catalysis.

In the course of the work in concentrated bromine solutions, two solid pyridine-bromine complexes were isolated. The first of these is very unstable; a molecular composition corresponding to $C_5H_5NHBr(Br_2)_2$ has been postulated. The second compound is more stable; the stoichiometry of this compound was found to correspond to $(C_5H_5NHBr_3)_2C_5H_5NHBr$.

Contrary to the work of Nelson and Iwamoto (50), strong evidence has been presented that the trihalide ions exhibit the same order of stability in the aprotic solvent chloroform as they do in water, i.e. $I_3^- > Br_3^- > Cl_3^-$.

TO MY PARENTS

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I. INTRODUCTION

There are a large number of references in the literature to pyridine catalysis in aromatic halogenation, but no definite documentation as to how pyridine causes this catalysis or as to how effective a catalyst pyridine is. The present study was undertaken to explore this subject and to lay the groundwork for discovering the mechanism of pyridine catalysis.

It was decided to concentrate on the bromination reaction in this research as bromine is easier to handle than chlorine and because the original work (17) on this subject indicated that bromination gives a higher yield of product. Work was carried out in both concentrated and dilute solutions of bromine, with and without a solvent. Early in the project it was realized that any catalytic activity pyridine possessed was because of its salts. Consequently most of the latter part of the project was concerned with the salts of pyridine and other amines (for comparative purposes).

Benzene and tert-butylbenzene were employed in the dual roles of substrate and solvent in the work with concentrated bromine solutions. Solid complexes containing pyridine and bromine were isolated and investigated in the course of the work with concentrated bromine solutions. In the work with dilute bromine solutions most of the experiments were done in the solvents acetic acid and chloroform. Other solvents employed were water, benzene and ethylene chloride.

To aid in planning and interpretation of the rate studies, equilibrium constants between tetrabutylammonium bromide and bromine and between pyridinium bromide and bromine were determined in chloroform. In the course of the equilibrium constant studies interesting results were found regarding the stability of trihalide salts.

II. HISTORICAL REVIEW

A. PYRIDINE CATALYSIS IN AROMATIC HALOGENATION

Cross and Cohen (17), in 1908, were the first to claim that pyridine was a catalyst in aromatic halogenation. In this very short publication their only remark regarding pyridine catalysis is that some work they did, concerning the halogenation of pyridine bases through their additive compounds with halogens, "suggested the possibility of employing these bases as halogen carriers, an anticipation which has been confirmed by the following experiments." This paper includes the pyridine-catalyzed bromination of benzene, bromobenzene, toluene, p-chlorotoluene and naphthalene. The chlorination of benzene and toluene is described. No experiments were done without pyridine bases for comparison, and no indication of the purity of source of the chemicals was given. Very few experimental details were included. As an example, their description of the bromination of benzene to bromobenzene follows.

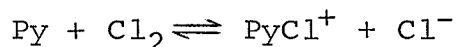
"A few drops of pyridine were added to a mixture of 50 grams of benzene and 120 grams of bromine, which were warmed to 25° in the water-bath. The action proceeds vigorously with the evolution of hydrogen bromide. The temperature was finally raised to 65-70°. The crude product, which boiled at 148-158°, amounted to 60 grams. The same result was produced with quinoline and isoquinoline."

Later, Cohen, in his well known laboratory manual (14), gave directions for brominating benzene to bromobenzene

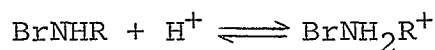
in the presence of pyridine. With respect to pyridine the method is only more specific in that 0.5 grams of pyridine are called for instead of a few drops. The quantities of benzene and bromine used are the same. Cohen, in the laboratory manual, accounted for the catalysis as follows. "The pyridine acts as a 'halogen carrier', probably by forming the additive compound, $C_5H_5NBr_2$, which gives up its bromine to the benzene."

Since Cohen's work several references to pyridine catalysis in aromatic halogenation have appeared. For example, in a brief survey the author found the following books, which referred to the catalytic effect of pyridine in aromatic halogenation. W. J. Hickinbottom in his book Reactions of Organic Compounds (31) lists pyridine as an available catalyst for bromination or chlorination of the aromatic nucleus. Sidgwick's Organic Chemistry of Nitrogen (67) states "Pyridine forms an efficient carrier in the chlorination and bromination of aromatic hydrocarbons". The following is quoted from An Introduction to the Chemistry of Heterocyclic Compounds (2) by R. M. Acheson. "The IR absorption spectra of solutions of iodine in pyridine suggest that 1-iodopyridinium iodide is obtained. If similar compounds are formed with bromine and chlorine, the catalytic effect of pyridine on halogenations such as the bromination of benzene is understandable. The pyridinium cation could be a more ready source of positive halogen than the halogen molecule itself." De la Mare and Ridd in their book Aromatic Substitution make reference three times

(20a, b, c) to pyridine being a catalyst. In the first instance they give a description of the bromination of tert-butylbenzene catalyzed by pyridine. Later they state, "The fact that pyridine and other tertiary amines act as powerful catalysts for chlorination and bromination suggests that ions of the type PyCl^+ , formed by equilibria of the type shown in the equation,



may be effective halogenating agents." The third instance reads, "There is in principle every reason to believe also that N-bromo-amides and -anilides can act as brominating agents through their protonated forms:



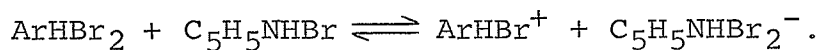
Presumably it is for such a reason that pyridine acts as a catalyst for bromination, but there is no definite documentation of this mechanism." It is interesting to note that not one of the above books gave any reference to pyridine being used as a catalyst in the literature nor offered any proof that it was, indeed, a catalyst.

There has been no detailed discussion of pyridine catalysis in aromatic halogenation, but the following references have been encountered in the literature and indicate the general views on this subject. Acheson, Hoult and Barnard (3) state "N-bromopyridinium bromide may be the source of bromine cations in pyridine-catalyzed brominations." They give no reference for their statement and did not do any work to support it.

Eisch and Jaselskis (22) state that "the catalytic role of pyridine in aromatic bromination has been ascribed to the intermediate N-bromopyridinium bromide serving as a source of bromine cations." They refer to the paper of Acheson, Hoult and Barnard mentioned above. Again no definite proof is presented that pyridine or quinoline could serve in the role suggested above. Longstaff and Singer (44) refer to pyridine and "its known catalytic effect in bromination reactions." They give three references to support their statement. One reference is to the original work of Cohen (17). A second reference is to the work of Rosenmund and Kuhnhenh (61) who used bromine addition compounds of pyridine and quinoline as mild brominating agents, but said nothing about these amines being catalysts in the positive sense. The third reference is to a publication of Krause (43). Krause used a bromine addition product of pyridine as a mild brominating agent in the preparation of triaryl tin halides. Longstaff and Singer in their own work used pyridine as a catalyst in the oxidation of formic acid by bromine. Pershina and Borodina (56) found that pyridine facilitated the iodination of phenols. De la Mare and Harvey (19) used pyridine as a catalyst for bromination in the synthesis of an aryl bromide. As a reference to the use of pyridine they give the work of Cohen.

The first kinetic study on the effect of pyridine was done by Yeddanapalli and Gnanapragasam (76) in 1959. They state that pyridine is considered to be a "halogen carrier"

and "is known to be a good catalyst for the bromination of aromatic compounds." Reference is given only to Cohen's laboratory manual. Yeddanapalli and Gnanapragasam studied the effect of pyridine on the rate of bromination of anisole in carbon tetrachloride. They found catalysis for concentrations of pyridine lower than and equal to the bromine concentration. For a concentration of pyridine ten times the bromine concentration, retardation was found. The following explanations were offered to account for their results. They attribute the catalytic effect to pyridinium bromide formed from pyridine in the course of the reaction. Pyridinium bromide was considered to increase the rate by intervention in the rate-determining step, the decomposition of the complex between bromine and the aromatic compound



The slow rate with excess pyridine was attributed to a decrease in the concentration of free bromine because of formation of $\text{C}_5\text{H}_5\text{NBr}_2$.

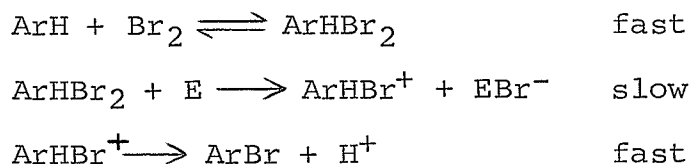
More recently a study of the effect of pyridine as a catalyst was reported by Tronov and Loginova at a conference in the U.S.S.R. The following is the translation of the abstract of this paper* as presented in Referativnyi Zhurnal, Khimia (68).

* The University of Manitoba Library was unable to obtain a copy of this. It was found that there are no Canadian or American holdings of the above conference proceedings.

"The catalytic activities of iron and pyridine in benzene bromination were compared. Iron was twenty times more active. Without a catalyst the reaction rates depended on the bromine concentration." This translation is also to be found in the Chemical Abstracts (68).

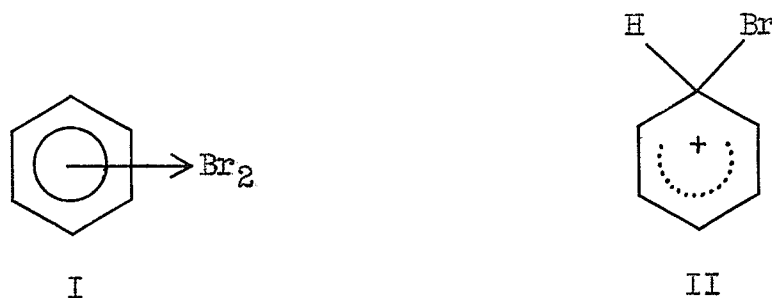
B. THE MECHANISM OF AROMATIC BROMINATION

The currently popular mechanism (51, 77) for the bromination of aromatic substrates (with the exception of very reactive or very sterically hindered compounds) by molecular bromine is the following.



This mechanism is consistent with all the information about the reaction obtained to date.

It is popularly accepted that complexes of the stoichiometry ArHBr_2 exist in solution; they are regarded as being charge-transfer or pi complexes (5, 7, 24). They are conventionally represented as in structure I in order to indicate that the bonding is of a weak nature and that the halogen is not attached to any definite carbon atom, but to the whole pi electron cloud.



The complex ArHBr^+ is commonly accepted (7, 52, 65) as being a sigma complex. Whereas in a pi complex the electronic system of the aromatic ring is regarded as being only superficially disturbed, it is considered that the electrophile has penetrated more deeply into the aromatic system in the sigma complex and that the electrophile is attached to a specific carbon atom by an electron pair originally belonging to the aromatic ring (7). The conventional representation for a sigma complex of this stoichiometry is structure II.

Ferguson (24) suggests that when an arene-halogen pi complex converts to a sigma complex, the interhalogen bond gets weaker and longer as the arene-halogen bond gets stronger. He quotes experimental evidence to support this.

The first step in the above mechanism is the rapid, reversible formation of the ArHBr_2 complex. The second step is the rate-limiting heterolysis of this complex. In the solvents of low polarity in which this reaction is ordinarily carried out, it is to be expected that this complex would not

ionize readily. This heterolysis is considered to be aided by the species E, when it does not take place in an unassisted manner. In acetic acid the order with respect to bromine is mixed first, second and third. The order is reduced, somewhat, by increasing the temperature, by adding water to the solvent, using lower bromine concentrations, or by adding salts (52, 20d). For example, the bromination of fluorene (77) in 75% aqueous acetic acid in the presence of excess bromide ion, which would both lower the bromine concentration and provide a salt effect, is found to be second order over-all, first order in each reactant. In glacial acetic acid this bromination is between second and third order in bromine when using a bromine concentration of 0.05 to 0.1 M. These results are aptly explained by the above mechanism. The first-order-in-bromine term represents an unassisted heterolysis or a heterolysis facilitated by the solvent or other species present in the solution. The higher order terms represent the incursion of one or two molecules of bromine acting in the role of E.

Norman and Taylor (51) believe that the higher polarity produced by the addition of water and salts is sufficient to permit the heterolysis to take place unassisted. Similarly Zimmerman and Berliner (77) have pointed out that water should not be pictured as taking the place of the second bromine molecule in a stoichiometric sense, because it is less electrophilic than bromine, and that the ions are formed more readily

because of the more favourable medium. They believe that this unassisted ionization is also possible to some extent in pure acetic acid.

On the contrary, Josephson, Keefer and Andrews (35) picture an acetic acid molecule functioning as the reagent E by hydrogen bonding to the departing bromide ion. They found that bromination was second order with respect to bromine in chloroform. The absence of a detectable first-order-in-halogen term was accounted for on the basis that chloroform cannot assume the specific role played by acetic acid in promoting the bromine-bromine bond break. The much lower rate constant in chloroform for the second-order-in-bromine reaction was attributed largely to the difference in dielectric properties of the two solvents.

Keefer, Ottenberg and Andrews (39) found that both the first-order-in-bromine and the second-order-in-bromine reactions were strongly accelerated by several different salts, but that the salt effect was more marked for the first-order than for the second-order reaction. Keefer and Andrews (38) observed that changing from pure acetic acid to 90% aqueous acetic acid results in 800-fold and 90-fold increases in the first-order-in-bromine and the second-order-in-bromine rate constants, respectively. They then considered whether these increases resulted entirely from dielectric effects or whether they represented in part a medium effect related to the hydroxylic

character of the solvent. The results of three rate runs on the bromination of mesitylene in chlorobenzene, a solvent with approximately the same dielectric constant as acetic acid, supported the latter view. In chlorobenzene the reactions were essentially pure second order in bromine, and this rate constant was much less than that found in acetic acid. In the same publication they examined the degree to which the rate of bromination of mesitylene was controlled by the capacity of the solvent to solvate bromide ion through hydrogen bonding. The first-order-in-bromine rate constant decreased by a factor of approximately 2 on changing from acetic acid to acetic-d acid; by 18% on changing from acetic acid to acetic-d acid in the presence of 0.245 M sodium perchlorate; by 23% on changing from 90% acetic acid-10% H₂O to 90% acetic-d acid-10% D₂O in the presence of 0.099 M sodium acetate. The authors state that these isotope effects are large enough to suggest that the H-O bond of the solvent is weakened, but not ruptured, in the rate-determining step. However it may be pointed out that the small magnitude of these changes in the rate constant suggests that the large increase in the first-order-in-bromine rate constant on addition of water is more a result of the more polar medium than it is a result of direct intervention in the rate-determining step via hydrogen bonding.

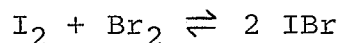
High-order bromination has also been observed in other solvents of low dielectric constant, such as carbon tetrachloride, methanol, and benzene (8).

The last step of the above mechanism is the rapid loss of the proton. This is supported by the lack of kinetic hydrogen-isotope effect in this reaction (47), with the exception of a few very reactive or sterically hindered substrates (78). That the last step is not rate-limiting is supported by the lack of any appreciable basic catalysis by sodium acetate (8).

Experimentally, kinetic studies of aromatic brominations are very complex. In addition to the mixed orders observed, the reaction is complicated by the formation of bromide ion. As a result bromine is continuously removed from the reaction as tribromide ion which has no, or only very weak, brominating properties (51). In order to avoid these difficulties many workers have based relative reactivities on the time required to achieve a given per cent reaction under a standardized set of reaction conditions (11). Other experimenters have avoided these difficulties by working with a large excess of bromide ion (77).

No other single kinetic scheme than the one given above will account for all the data obtained on bromination. However, the data can be accounted for reasonably well if one invokes different mechanisms for the first-order-, the second-order- and the third-order-in-bromine reactions, and is willing to attribute an important role to the species Br_4 . These other schemes, while not as rational, can not be ruled out kinetically. These schemes can be found in the following references (8, 77).

Various substances can be used to catalyze aromatic bromination which clearly have more than a medium effect. One of the most common of these is molecular iodine. Iodine bromide is formed according to the following equation in which the equilibrium lies well to the right (51).



In the accepted mechanism (51) for iodine catalysis IBr takes the place of the species E in the second step of the above mechanism, thus aiding in the heterolysis of the bromine-bromine bond of the ArHBr_2 complex. IBr will be more efficient than Br_2 in this role because of the greater ease with which iodine expands its octet to form such ions as IBr_2^- . The mechanism described above for aromatic bromination is supported by this catalysis by IBr and is also consistent with the fact that high orders of reaction are not observed with chlorine (20d); this halogen cannot so readily form anions like Cl_3^- .

Gould in his book Mechanism and Structure in Organic Chemistry (28) is in agreement with the viewpoint that for halogenations with molecular halogen and a catalyst the most likely mechanism is for the catalyst to assume the role of species E in the mechanism presented earlier. He states that halogens, carboxylic acids, water and metallic halides may act in this role of electrophilic catalyst. Intervention by halogens in the rate-determining heterolysis has been discussed above. The possibility of water and acetic acid acting in this role has also been considered. However, since Mechanism and Structure in Organic Chemistry was written, evidence has been presented (36, 53) that metallic

halides do not catalyze bromination in this manner and, furthermore, that the mechanism is considerably altered when they are involved. An example of this evidence, given below, indicates that ferric chloride is capable of making the halogen sufficiently electrophilic that heterolysis of the bromine-bromine bond is no longer kinetically important and that the over-all rate is much faster.

Olah, Kuhn, Flood and Hardie (53) studied the ferric chloride catalyzed bromination of benzene and alkylbenzenes with bromine in nitromethane solution. Relative reactivities and isomer distributions were determined. The low substrate selectivity observed, in comparison to molecular and acidified hypobromous acid brominations, is indicative of a highly electrophilic brominating species. "The isomer distributions seem to be characteristic for electrophilic aromatic substitution involving only small steric effects (incipient Br^+ as compared with Br_2 which displays a substantial steric effect)." No kinetic hydrogen-isotope effect could be detected in this work. Relative rates showed agreement with π but not sigma complex stabilities of the investigated alkylbenzenes. This is further evidence that this bromination is not typical of ordinary brominations, as the relative rates of the latter correlate with sigma complex stabilities (53). Further, the authors propose that the correlation with π complex stabilities indicates that the reactions involve a π complex type transition state in the substrate selectivity-determining step, followed

by lower energy level transition states of sigma complex nature, determining positional selectivity. They regarded the brominating species as a strong electrophile - incipient, if not necessarily free, bromonium ion.

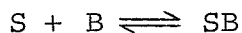
C. DETERMINATION OF EQUILIBRIUM CONSTANTS

Several methods for the determination of equilibrium constants are available. These methods include diffusion, dialysis, solubility measurements, distribution measurements, potentiometry, polarography, conductometry, amperometry, spectrophotometry, refractometry and ion-exchange techniques (62).

A spectrophotometric method was chosen for the equilibrium constant determinations in this research project. This selection was made because spectrophotometric methods are most commonly used for equilibrium constant determinations of the type involved in this work. Furthermore this technique was more convenient as spectrophotometry was also used for some of the reaction rate measurements.

Various spectrophotometric methods of determining equilibrium constants are available (10, 62). The most commonly used in work similar to that presented in this thesis is the Benesi-Hildebrand method (6). This method is just a special case of the more general Rose-Drago technique (60). The following is a derivation of the latter method.

If two species interact in solution to form a complex according to



and if the absorption spectrum of SB is markedly different from the sum of the spectra of free S and B, it is usually possible to determine the equilibrium constant by a spectrophotometric method. The equilibrium constant expression for this reaction is

$$K = \frac{C}{(S_0 - C)(B_0 - C)} \quad (1)$$

where C = the concentration of complex SB at equilibrium; S_0 and B_0 are the initial concentrations of S and B. The absorbance of such a solution will be given by

$$A = E_c C + E_s (S_0 - C) + E_b (B_0 - C) \quad (2)$$

where E_c , E_s and E_b refer to the absorptivity of SB, S and B respectively. Grouping and rearranging 2 allows the concentration of complex to be expressed as

$$C = \frac{A - E_s S_0 - E_b B_0}{E_c - E_s - E_b} .$$

For simplification substitute

$$D = A - E_s S_0 - E_b B_0$$

and
$$E = E_c - E_s - E_b .$$

Then
$$C = D/E .$$

On expanding and inverting equation 1 the following is obtained.

$$1/K = S_0 B_0 / C - S_0 - B_0 + C$$

On substituting in D/E for C the result is

$$1/K = S_0 B_0 E/D - S_0 - B_0 + D/E. \quad (3)$$

This equation is the same as that originally derived by Rose and Drago (60) except that they derived the equation for the experimental conditions in which only one of the reactants absorbs.

When the experimental conditions are such that $D/E - B_0$ is negligible compared to $S_0 B_0 E/D - S_0$ equation 3 reduces to

$$1/K = S_0 B_0 E/D - S_0. \quad (4)$$

This on rearrangement gives

$$S_0 = E S_0 B_0 / D - 1/K. \quad (5)$$

Equation 5 is one of several modifications of the well known Benesi-Hildebrand equation (6, 40, 63). Equation 4 can also be arrived at by taking $S_0 \gg B_0$ so that S_0 can be substituted for $(S_0 - C)$ in equation 1. A follow-through of the above derivation then leads directly to equation 4 at the step where equation 3 was obtained previously.

However, even though equation 4 can be derived by taking $S_0 \gg B_0$, it has been shown (60) that $S_0 \gg B_0$ is not always a sufficient condition for the validity of equation 4. If the difference between $S_0 - C$ and $S'_0 - C'$ (where the prime values correspond to a second set of S concentrations) is not very large the magnitude of C and C' may be important to the final solution even though $S_0 \gg B_0$. This has been discussed more fully in the above reference. The validity of equation 4 must

be determined by comparison of the magnitude of $D/E - B_0$ and $S_0B_0E/D - S_0$.

Equation 5 has an obvious advantage over equation 3 in that it is easier to use. Plotting S_0 versus S_0B_0/D according to equation 5 yields a straight line. From the intercept and slope of the straight line the formation constant and the absorptivity of the complex can be calculated. This formation constant and absorptivity can be obtained from equation 3 by algebraic solution of the various sets of simultaneous equations. Alternately, the common graphical method of solution of simultaneous equations can be employed. As all pairs of equations, theoretically, give the same value of $1/K$ and E they can all be plotted on the same graph and the coordinates of the common point of intersection constitute the solution.

Rose-Drago equations for stoichiometry other than 1 : 1 can be derived and treated similarly. The assumptions implicit in all of the above derivations are that there are at most three absorbing species which obey Beer's law in the concentration range employed. K is not a thermodynamic constant as activity coefficients are not taken into account.

Much criticism has been aimed at the use of these methods of equilibrium constant determination. The Benesi-Hildebrand method and the use of it has received the most criticism. A

study (60) has disclosed that it has been used in several instances in the literature where its approximation to the Rose-Drago equation was not valid.

The Benesi-Hildebrand equation has been shown (13) to give erroneous results for weak complexes because it does not take into account the competition between complexing by the solvent and complexing by the species being studied. A very recent study (69) has re-emphasized this and pointed out another difficulty which occurs in the determination of weak complexes. In the experimental work involving weak complexes it is necessary to use such high concentrations that it is no longer valid to assume the solutions behave ideally; this results in large errors in K . Even excellent linear plots do not prove that the solution is behaving ideally and that the solvent is not complexing significantly. These criticisms would also apply to the Rose-Drago equation and any other techniques which do not make the appropriate allowances. This will not be discussed further as the complexes examined in this study were by no means weak.

W. B. Person (57) has suggested a reliability criterion for Benesi-Hildebrand determinations. His work shows that the most accurate values of equilibrium constants are obtained when the equilibrium concentrations of the complex and the more dilute component are of the same order of magnitude. This can be illustrated as follows. Following Person, the situation

where only the complex absorbs will be dealt with in order to simplify the discussion. Person used a rearranged form of equation 5 to base his discussion on. However, the following discussion is adapted to pertain to equation 5, as this equation was used in some of the work discussed in this thesis. The symbols to be used here have the same meaning as they did in the derivation of equation 5.

As we are now considering the situation in which only the complex absorbs, equation 2 simplifies to

$$A = E_c C$$

and E/D in equation 5 becomes E_c/A , thereby converting equation 5 to

$$S_0 = E_c S_0 B_0 / A - 1/K. \quad (6)$$

The absorbance A is given by

$$A = E_c C = E_c K (S_{eq}) (B_{eq})$$

where (S_{eq}) and (B_{eq}) are the equilibrium concentrations of S and B respectively. As $S_0 \gg B_0$ is a necessary condition for equation 6 to apply we have that (S_{eq}) is approximately equal to S_0 . Now, if the concentration of S is not high enough, the concentration of the complex will be very small so that (B_{eq}) is approximately equal to B_0 . This results in

$$A \cong E_c K S_0 B_0.$$

It can be seen that interpretation of data, according to equation 6, under these concentration conditions results in an intercept at infinity. This indicates a formation constant of 0, even though it may be significantly larger. On the other

hand, when the concentration of S is so large that virtually all of B is complexed we have that

$$A \cong E_c B_0.$$

Interpretation of data under these concentration conditions results in a straight line passing through the origin. This indicates a formation constant of infinity, even though the true value is finite. To avoid both of these undesirable concentration conditions it is necessary to select experimental concentrations such that the equilibrium concentrations of the complex and the more dilute component are of the same order of magnitude. This limitation on the concentration range once again points out the large errors possible in attempting to determine the equilibrium constants of weak complexes, as the requisite concentration range may be higher than that permitted by practical considerations of solubility.

P. R. Hammond (30) has examined the effect of errors in absorbance and concentration on different forms of the Benesi-Hildebrand equation. He found that errors in the formation constant and absorptivity of the complex increased markedly for decreasing formation constants.

Johnson and Bowen (34) have shown that, contrary to popular belief, linearity of Benesi-Hildebrand plots does not constitute proof that only a 1 : 1 complex exists. They demonstrated with the aid of synthetic data that the presence of a 1 : 2 or a 2 : 1 complex did not lead to such significant

variations from linearity that the presence of a second complex would be indicated.

Conrow, Johnson and Bowen (15) have shown that even with synthetic data free of all experimental error the resulting value of K can still be out by more than 10% when using their computer technique or the Rose-Drago equation. The introduction of small errors into the synthetic data revealed the results to be extremely sensitive to errors in the input data. This inherent indeterminism can be shown to result from the poor choice of experimental conditions. Their analysis of the situation indicates that the conditions necessary to minimize the effects of errors are dependent on the particular system being studied. They give the following general conditions for accurate determination of equilibrium constants: (a) The slopes of the plots of $1/K$ and E must differ from each other by as much as possible. (b) The errors in the concentrations must be reduced to the point that their contributions to the errors in the slopes will be small compared to the variations between the slopes. (c) In order to minimize errors in the displacement of the curves, a region of the spectrum should be chosen in which the contribution of the complex to the observed absorbance is large.

D. THE TRIHALIDE ION

Excellent reviews (64, 73) have been published on this subject and the following material, unless otherwise indicated,

is taken from these reviews.

All the trihalide ions that can be formed by chlorine, bromine and iodine have been shown to be formed, not only in the solid state but also in solution. However the trifluoride ion has not been reported (presumably because fluorine cannot expand its octet to accommodate the requisite number of electrons). X-ray evidence, obtained from the solid salts, indicates that the ion is linear, with the heaviest atom in the middle.

The information presented in this paragraph is based on experimental data obtained in aqueous solutions. The order of stability for trihalide ions consisting of one species is $I_3^- > Br_3^- > Cl_3^-$. In general, the stability of the trihalide ion increases with increasing atomic weight of the central atom. The effect of the outer atoms is less predictable, but the stability seems to be greater (a) the nearer the terminal atoms are in mass to the central atom and (b) the nearer they are to one another. As an example of (a) we have that IBr_2^- is more stable than ICl_2^- . An example of (b) is the greater stability of $IBrCl^-$ in comparison to the stability of I_2Cl^- .

The relative stability of the solid trihalides has been determined by measuring the temperature at which the dissociation pressure reached one atmosphere, and from the concentration of the halogen (pure or mixed) dissolved out from the solid salt by such a solvent as carbon tetrachloride. When the stabilities

of trihalides containing the same trihalide ion but different cations were compared, it was found that the stability is greater when the cation is larger and more symmetrical. For solid trihalides containing the same cation but different trihalide ions it is again found that the order of stability is $I_3^- > Br_3^- > Cl_3^-$.

In 1964 Nelson and Iwamoto (50) compared the stabilities of the trihalides in nitromethane, acetone and acetonitrile by a voltametric method. In all of these solvents they found the order of stability to be $Cl_3^- > Br_3^- > I_3^-$. This is opposite to the order found in water and opposite to the order observed in the solid salts (64). They state that the expected order is as they have observed. Their rationale for this is as follows. "Because the acid strength, in the Lewis sense, of the three halogens is chlorine > bromine > iodine and the basic strength of the three halides is chloride > bromide > iodide". They account for the order observed in water being the reverse on the basis that water "is a stronger acid than chlorine and a stronger base than chloride ion: therefore, the hydration of both X^- and X_2 increases from the triiodide system to the trichloride system and the stability of the trihalides, accordingly, decreases in the order triiodide > tribromide > trichloride."

The rest of this discussion of trihalide ions deals specifically with the tribromide ion as it is more important to the main theme of the thesis. Several experimenters have

determined formation constants for the tribromide ion in water, acetic acid and in various mixtures of these two solvents. The two most informative references are the following, wherein are given all the other pertinent references. In 1957 Nakagawa, Andrews and Keefer (49) presented a plot of the formation constants of the tribromide ion at 25.0° C versus the volume % acetic acid of acetic acid-water mixtures. The authors used a spectrophotometric method and determined all of the experimental points with the exception of that at 0% acetic acid, which was taken from the literature. In 1960 Daniele (18) published a list of experimental values, determined by various researchers using different methods, for the formation constants of the tribromide ion in acetic acid, water and mixtures of the two solvents. Daniele re-determined the value for pure water by a spectrophotometric method. The following is a brief summary of the data presented in the above two references. The formation constant in pure water is approximately 20 litres/mole with the constant gradually increasing with increasing acetic acid content until ca. 95% acetic acid is reached, after which there is a decrease in the value. The formation constants are essentially independent of whether the bromide source is NaBr or HBr until the acetic acid content of the solvent exceeds 90%. For larger percentages of acetic acid a larger constant is obtained with HBr. Using HBr the formation constant is ca. 190 and 125 litres/mole for 95% and 100% acetic acid, respectively. For NaBr the formation constant is ca. 135

and 55 litres/mole for 95% and 100% acetic acid, respectively.

As mentioned above, Nelson and Iwamoto (50) have determined formation constants of the tribromide ion in aprotic solvents. The complex between tetraethylammonium bromide and bromine is reported by them to have thermodynamic formation constants of $10^{7.3}$, $10^{9.3}$ and 10^7 in nitromethane, acetone and acetonitrile, respectively, as determined by a voltametric method.

III. METHOD AND RESULTS

A. METHOD AND RESULTS IN CONCENTRATED BROMINE SOLUTIONS

1. Re-investigation of the Work of Cross and Cohen and Related Studies

Cross and Cohen (17) in their work did not actually determine if pyridine catalyzed aromatic halogenation as they did no experimental work without pyridine for comparison. Preliminary investigation of the original work of Cross and Cohen in a qualitative manner verified that pyridine did catalyze the bromination of benzene. In two experiments conducted simultaneously under the Cohen conditions at approximately 25°C, but one with pyridine and one without, it was observed that hydrogen bromide was evolved at a greater rate in the trial involving pyridine. Simple distillation of the organic material separated from the reaction mixtures indicated there was considerably more bromobenzene after a four hour period when pyridine was used.

In the reaction mixture containing pyridine a dark red solid precipitated, henceforth to be referred to as I. In subsequent work this material was isolated and investigated. On washing with carbon tetrachloride at room temperature, I turned into an oil, which in turn formed an orange solid to be referred to as II. It was found that I kept fairly well for 24 hours at approximately -20°C. When I was left at room temperature it gradually decomposed over a 15 minute period to

give a liquid which seemed to contain some solid as well. This material turned completely into an orange solid on standing over night. As would be expected this orange solid was identical with II, both having the same melting point with no depression on mixing when melted simultaneously in the same apparatus. The melting point was found to vary with the rate of heating. Values such as 100-105, 94-103 and 99-110°C were obtained.

A bromination under the Cohen conditions was carried out, substituting II for pyridine. A blank run in which II was omitted was done simultaneously. Judging by the evolution of hydrogen bromide and a crude density determination of the organic products obtained in the two runs, II also catalyzed the bromination of benzene. In the trial in which II was added, a dark red solid precipitated, identical to I in appearance and instability.

It was also noted that when I was added to a mixture of benzene and bromine in the concentrations employed by Cohen catalysis took place, as manifested by a very large increase in the rate of hydrogen bromide evolution. In a separate trial, it was found that the rate of the reaction decreased greatly on filtering I out of solution. In another trial it was observed that on warming a reaction mixture to about 35°C, I appeared to dissolve.

Having noted that I appears to dissolve on warming to 35°C as mentioned above, it was decided to investigate at this

temperature the effect of pyridine and some salts on the rate of bromination under the high bromine concentrations employed in the Cohen conditions. Tert-butylbenzene was used as both substrate and solvent. The rates were followed by iodometric analysis of bromine. The errors were of course large, because of the high volatility of bromine at such concentrations, but the results are of qualitative or semi-quantitative significance. Comparing the first 100 seconds of all reactions (this was ca. 50% reaction for the fastest reaction) when using the same concentration of reactants and the same concentration of pyridine or salt, the following approximate results were obtained. In the presence of pyridine, 15 times more bromine was consumed than in the uncatalyzed reaction; in the presence of pyridinium chloride, 7 times more; in the presence of pyridinium bromide and in the presence of tetrabutylammonium bromide, 10 times more.

On closer examination during this work it was found that in the pyridine case solution of I had not taken place, but that a small second layer was discernible at the bottom of the flask. A small second layer was also evident for all the runs employing salts. It was very difficult to see the second layer as both layers were the same color. When only the aromatic compound and bromine were present, only one layer existed. Because of this non-homogeneous medium the above relative rates may not be very meaningful.

2. Composition of the Complexes Isolated

Analysis of I for reducible bromine content gave a value of $70.0 \pm 0.2\%$ for three trials. The accuracy of this value is questionable because of the instability of the compound. As mentioned earlier, I decomposes on standing and on being washed. Therefore the compound had to be analyzed immediately and without being washed. The good precision of the analysis is probably because the procedure was repeated as exactly as possible each time. A possible molecular composition for I will be considered in the Discussion of Results.

Complex II was stable and a more rigorous approach could be taken towards determining its composition. The most likely possibilities for the composition of II, $C_5H_5NHBr_3$ (48) and $C_5H_5NBr_2$ (74), could be eliminated on the basis of melting points. However, a complex found in the literature, for which the experimenters (23) had been unable to assign a satisfactory formula, was a possibility as far as melting points were concerned. Hereafter this latter complex will be known as III. These experimenters found that III had a melting point of $101-103^\circ C$ and contained 39.7% reducible bromine. Essentially, III was prepared by mixing one mole of pyridine hydrobromide and one-half mole of bromine in glacial acetic acid.

As stated earlier, the melting point of II varied with the rate of heating. A sample of III was prepared and was found to have the same melting behaviour as II. The following

three samples, II, III and a mixture of II and III, were put in a melting point apparatus at the same time. On heating, all three samples melted at the same temperature and with the same behaviour. The near-IR spectra of II and III in ethylene chloride are the same. Analysis of the reducible bromine content for III gave a value of 40.1% and the same analysis for II gave a value of 40.6%. Thus it can be safely concluded that II and III are the same complex.

Knowing that II can be made from pyridine hydrobromide and bromine the initial assumption can be made that II is some complex of these two compounds. The NMR spectrum of II (Figure 1) in methylene chloride showed that II was not ring substituted and that a proton was present on the nitrogen atom. The IR spectrum of II (Figures 2 and 3) in methylene chloride is very similar to that of pyridinium bromide (Figure 2) but is greatly different from that of pyridine (Figure 3). Thus it can be safely said that all of the pyridine present in II is present as pyridinium bromide. A complex having a $C_5H_5NHBr : Br_2$ ratio of 1 : 1 would have a reducible bromine content of 50%. Therefore II, which has a reducible bromine content of 40%, has less than one molecule of bromine per molecule of pyridinium bromide. It is unlikely that this is just a conglomerate of C_5H_5NHBr and $C_5H_5NHBr_3$ because II sublimed under a vacuum of 2 or 3 mm. gives a product unchanged in melting point and appearance. Further analytical work was done to give more information regarding the composition of II.

FIGURE 1

Figure 1 is the proton magnetic resonance spectrum of saturated solution of II in methylene chloride with internal reference TMS (tetramethylsilane). The lower trace shows the compound proton spectrum on a scale of 500 CPS with the reference offset so that the length of the chart paper corresponds to the region from 400 CPS to 900 CPS (as is marked on the chart paper). The field increases from left to right.

The low field broad singlet resonating at about 740 CPS to low field of TMS corresponds to a NH^+ proton resonance signal. The magnitude of this shift is almost equivalent to the NH^+ proton shift observed by G. Kotowycz, T. Schaefer and E. Bock (Can. J. Chem. 42, 2541 (1964)) for pyridinium bromide in methylene chloride (after conversion to a TMS internal reference).

The high field peaks consist of three multiplets centred approximately at 530, 510 and 480 CPS to low field of internal TMS. The shifts obtained are nearly equivalent to the ortho, para and meta proton shifts respectively obtained by the above authors for pyridinium bromide in methylene chloride. This shows that II can not be ring substituted.

The upper trace shows the ring proton spectrum on an expanded scale of 100 CPS.

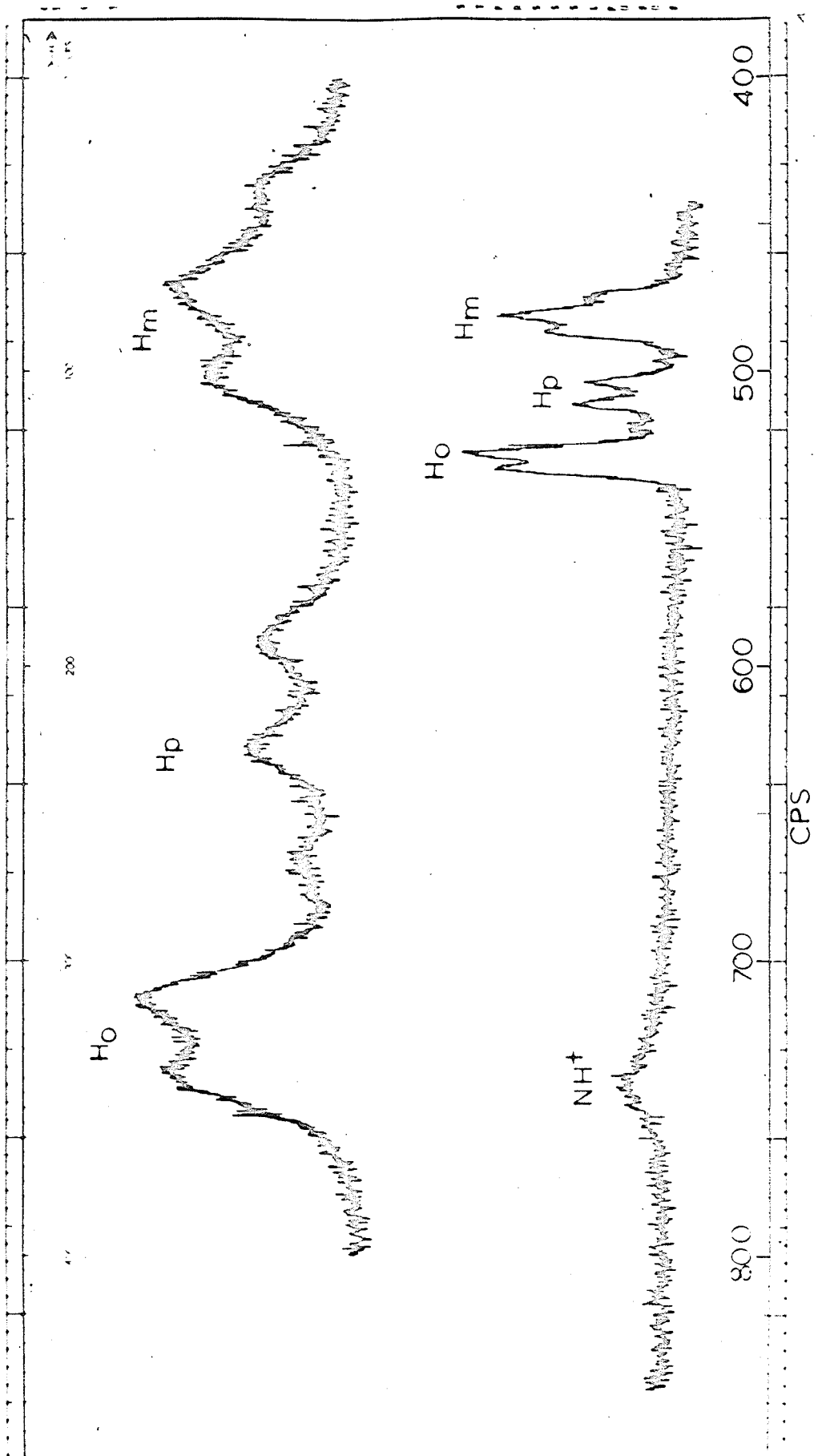


FIGURE 1

FIGURE 2

The upper trace is the IR spectrum of II in methylene chloride. The lower trace is the IR spectrum of pyridinium bromide in the same solvent.

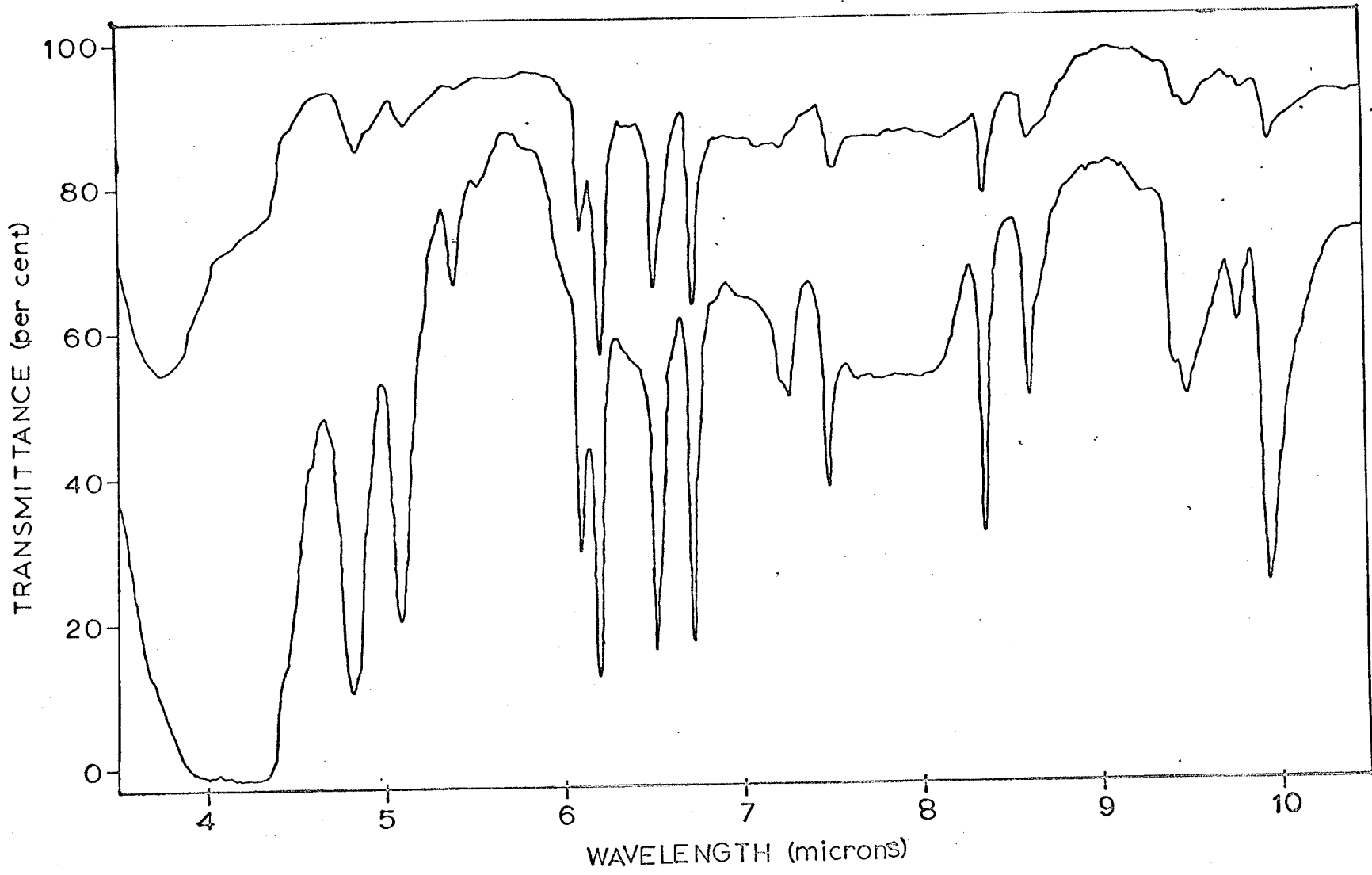


FIGURE 2

FIGURE 3

The broken line is the IR spectrum of II in methylene chloride. The other trace is the IR spectrum of pyridine in the same solvent.

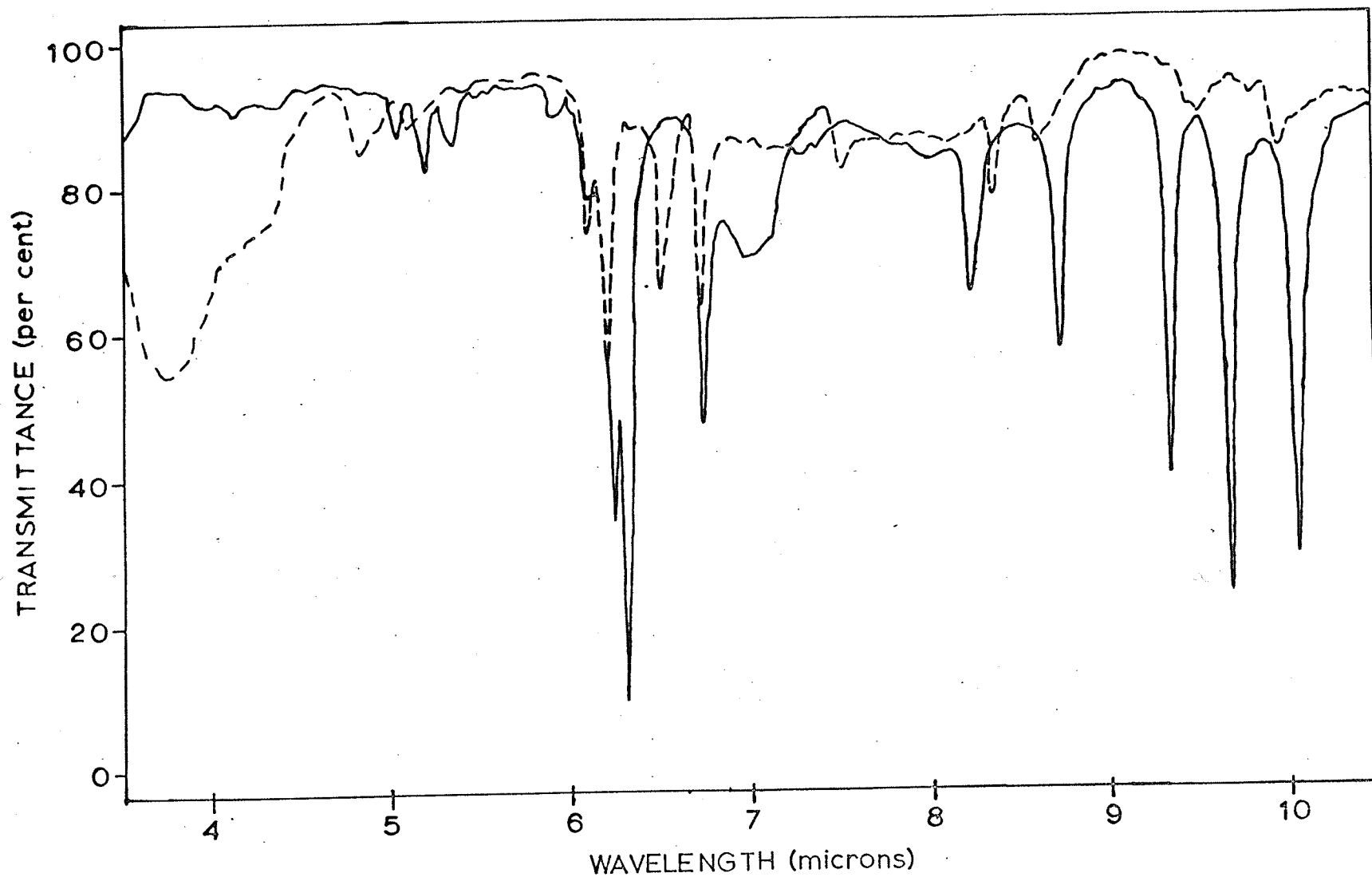


FIGURE 3

This work is given in the table below along with the calculated values for some molecular formulae of possible complexes of pyridinium bromide. The estimated experimental error in each determination is 1.5%. The results strongly favour the

TABLE 1

	M.W.	Neutral- ization Equivalent	% Reducible Bromine	% Total Bromine
$C_5H_5NHBrBr_2$	319.85	319.85	50.0	75.0
$(C_5H_5NHBr)_2Br_2$	479.87	239.94	33.3	66.6
$(C_5H_5NHBr)_3(Br_2)_2$	799.72	266.57	40.0	70.0
$(C_5H_5NHBr)_4(Br_2)_3$	1119.57	279.89	42.8	71.4
Experimental values for II		266.7	40.3*	70.0

* Average value obtained from II and III.

molecular formula $(C_5H_5NHBr)_3(Br_2)_2$.

3. Attempt to Prepare a Complex of Pyridinium Chloride and Bromine of Definite Composition

X-ray crystallography was considered as a possible means of gaining information regarding the structure of II. It was realized that a compound containing seven bromine atoms would cause considerable scattering and make analysis of the data very difficult. Therefore an attempt was made to make complexes of

pyridinium chloride and bromine in the hope that they would facilitate crystallographic work.

An early reference (70) gives accounts of pyridinium chloride being treated with bromine. It reports obtaining compounds that contained no chloride. Later workers (23, 45) have reported perbromides of pyridine hydrochloride and bromine, but have given neither melting points nor analyses.

In the work which is reported here, several attempts were made at preparing such complexes. Unlike II, the products were in all cases unstable and lost bromine on standing. The first try at preparing such a compound was an attempt to produce an analog of II, and a method very similar to that used in the preparation of III (addition of 1 mole of bromine to 2 moles of pyridinium chloride) was employed. A preliminary analysis of the product was carried out by potentiometric titration, employing a silver electrode, to determine if chlorine were present and, if chlorine were present, to establish the ratio of bromine to chlorine. The bromine to chlorine ratio was far too high for an analog of II and attempts to make the analog were abandoned. Preparation of the compound $C_5H_5NHClBr_2$ was then attempted. The best preparation was achieved by passing dry hydrogen chloride into a solution of $C_5H_5NBr_2$ in ethylene chloride. An orange solid with a melting point of 87-91°C was obtained. The reducible bromine content was 55.1%, whereas $C_5H_5NHClBr_2$ requires 58.0%. The low value obtained is probably

because of the instability of the compound. Because of this low stability this work was not continued further.

B. METHOD AND RESULTS IN DILUTE BROMINE SOLUTIONS

As it was not convenient to continue studying the effect of pyridine under the Cohen conditions because of the heterogeneity involved, consideration was given to its effect with low bromine concentrations where homogeneity would result.

1. Bromination in Benzene (Solvent also Serving as Substrate)

The initial amount of reaction was determined for four samples of benzene having identical bromine concentrations (ca. 0.15 M) and whose approximate pyridine concentrations were nil, 0.025 M, 0.12 M, and 0.5 M. The decrease in bromine content was determined by titration. As illustrated in Table 2, it was found that the higher the pyridine concentration the slower was the rate of reaction, the sample with no pyridine having the fastest rate.

TABLE 2

Per Cent Bromine Consumed in Benzene at ca. 22°C

Initial Br ₂ conc. 0.15 M	
Time reacted 11 hours	
<u>Pyridine conc.</u>	<u>% bromine consumed</u>
nil	4.9
0.025 M	2.3
0.12 M	1.6
0.50 M	0.6

In view of this unexpected result it was decided to see if the effect that pyridine had on bromination depended on the polarity of the medium. To test this, various solvents were employed.

2. Bromination in Water

o-Nitroanisole (ca. 0.005 M) was brominated in water solution (ca. 0.002 M in bromine). The addition of pyridine (ca. 0.002 M) retarded the rate in comparison to a trial in which no pyridine was used. The results are presented graphically in Figure 4.

3. Bromination in Acetic Acid

Preliminary work was concerned with testing for pyridine catalysis in aromatic bromination. In this work 0.075 M bromine was employed and concentrations of pyridine in the runs were nil, 0.06 M, 0.12 M and 0.25 M. Toluene (0.4 M) was the substrate. The results (shown graphically in Figure 5) indicate that pyridine is a catalyst but the results are rather unusual in one respect. It was found that the smallest amount of pyridine increased the initial rate the most and the largest amount increased the rate the least.

Subsequent work was planned to test the effect of pyridinium bromide on aromatic bromination. It was found that, at a concentration of 0.05 M in bromine and 0.3 M in *o*-xylene,

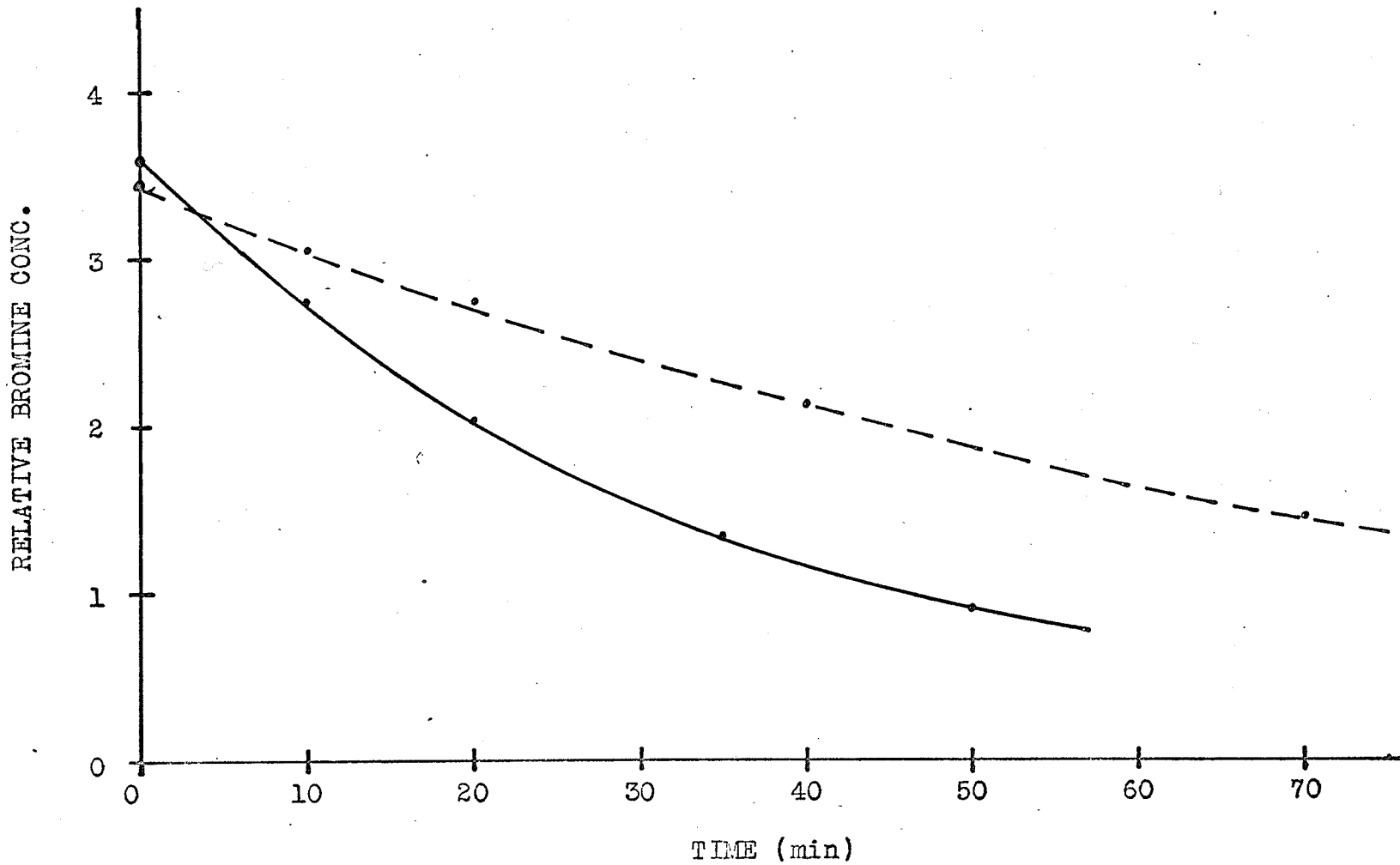


FIGURE 4

FIGURE 5

Figure 5 gives plots of the bromine concentration in arbitrary units versus time for the bromination of toluene in acetic acid. The toluene concentrations (0.4 M) and the bromine concentrations (0.075 M) were the same in each of the runs. The pyridine concentrations are as follows.

<u>+</u>	nil
<u>Δ</u>	0.06 M
<u> </u>	0.12 M
<u>o</u>	0.25 M

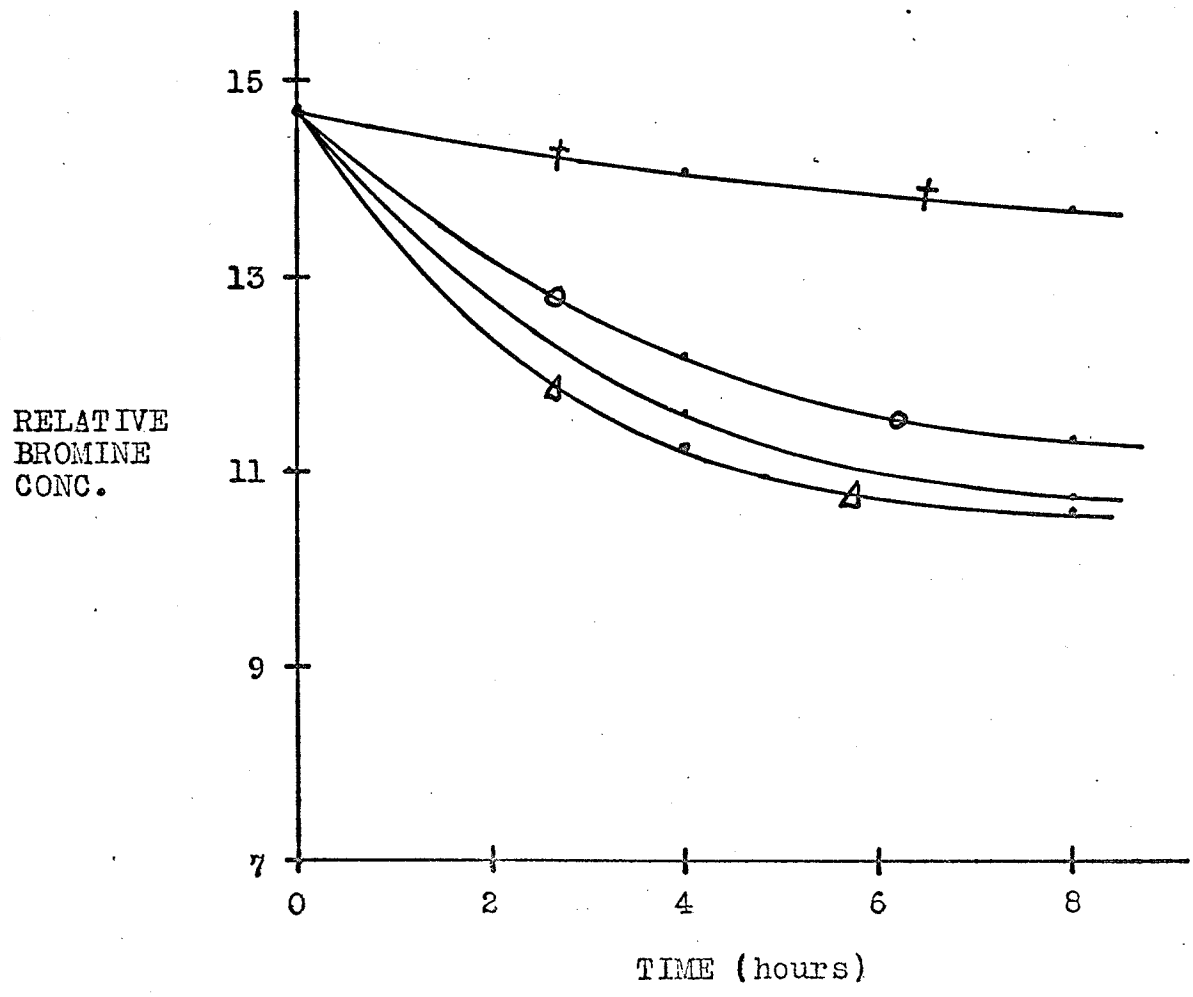


FIGURE 5

the addition of 0.125 M pyridinium bromide almost stopped the reaction in comparison to a blank run without pyridium bromide. In another trial with a different substrate (0.74 M in m-xylene) and at a lower bromine concentration (0.015 M) the addition of 0.06 M pyridinium bromide was found to increase the time for 10% reaction from ca. 30 minutes in the absence of pyridinium bromide to ca. 270 minutes.

The remainder of the data in acetic acid were obtained by following the loss of bromine spectrophotometrically. The substrate employed in this work was mesitylene. Bromination of mesitylene in acetic acid has been done previously by Keefer, Ottenberg and Andrews (39). These authors demonstrated that the only product formed in significant amount was 2-bromomesitylene. They used slightly different experimental conditions: a higher temperature (25.4°C compared to 25.0°C used in this study) and acetic acid containing more moisture (melting point of 16.2°C compared to 16.55°C for that used in this study). However, this is not of importance as the purpose of this work is to study the effect of different amine salts on the rate of bromination. This has not been previously examined. Bromine absorbances in the solutions used here were not precisely proportional to the total bromine concentration, but the deviations (about 5-10% over the absorbance ranges used) were not sufficient to invalidate the comparisons to be made as great accuracy is not required to obtain the desired information.

Keefer, Ottenberg and Andrews (39) state that the rate of disappearance of bromine from mesitylene solutions in acetic acid shows mixed first- and second-order dependence on total bromine concentration according to the following equation.

$$R = -dB/dt = k_2MB + k_3MB^2 \quad (7)$$

R is the rate, M and B are the concentrations of mesitylene and total bromine respectively in moles/litre and t is the time.

It can be seen from the work of the above authors that, for a concentration of 0.002 M bromine, less than 8% of the reaction can be attributed to the second-order term (first-order-in-bromine term). For the purposes of this study this small second-order contribution can be ignored.

Assuming a third-order reaction, the integrated rate expression (when mesitylene is in excess) is

$$1/B = k_3Mt + 1/a. \quad (8)$$

M, B and a are the concentrations of mesitylene, total bromine and initial total bromine respectively in moles/litre. t is the time and k_3 is the third-order rate constant. Also

$$A = eB.$$

A is the absorbance and e is the absorptivity of total bromine. e is determined from the absorbance at zero time and an iodometric determination of the initial bromine concentration. Combination of the above two equations gives

$$e/A = k_3Mt + 1/a. \quad (9)$$

Rearrangement yields

$$1/A = k_3Mt/e + 1/ae. \quad (10)$$

If the reaction is second order in total bromine a plot of $1/A$ versus t will give a straight line with a slope equal to k_3M/e . k_3 is calculated from this value.

A kinetic run with no added salt gave a fairly good straight line (Figure 6) when plotted as a third-order reaction, verifying that the contribution from the second-order reaction is small. The corresponding values of absorbance versus time are given in Table 3. The kinetic data for the rates with added salts also gave reasonably good straight lines, indicating that, here also, the reactions are predominantly third order. Typical data and a typical plot, that for pyridinium chloride, are given in Table 4 and Figure 7 respectively. A summary of the third-order rate constants for the work in acetic acid is presented in Table 5.

In general, this work proves that a pyridinium salt is no better catalyst than other amine salts.

4. Studies in Ethylene Chloride

Considerable effort was expended at trying to obtain results in ethylene chloride. Unfortunately success was not achieved. It was considered desirable to determine the effect of pyridine and pyridinium salts in an aprotic solvent of low polarity to approximate the Cohen conditions, and ethylene

TABLE 3

BROMINATION OF MESITYLENE IN ACETIC ACID

$$t = 25.0^{\circ}\text{C}$$

Initial concentrations: mesitylene 0.0479 M
bromine 0.00205 M

<u>Time (min)</u>	<u>Absorbance</u>	<u>1/Absorbance</u>
10.0	0.320	3.13
30.0	0.271	3.69
50.0	0.236	4.24
70.0	0.211	4.74
90.0	0.189	5.29
110.0	0.171	5.85
140.0	0.149	6.71
170.0	0.131	7.63
200.0	0.116	8.62

FIGURE 6

Figure 6 (a plot of the data of Table 3) gives a plot of $1/A$ ($1/\text{absorbance}$) versus time for the bromination of mesitylene in acetic acid.

Initial concentrations: mesitylene 0.0479 M
bromine 0.00205 M

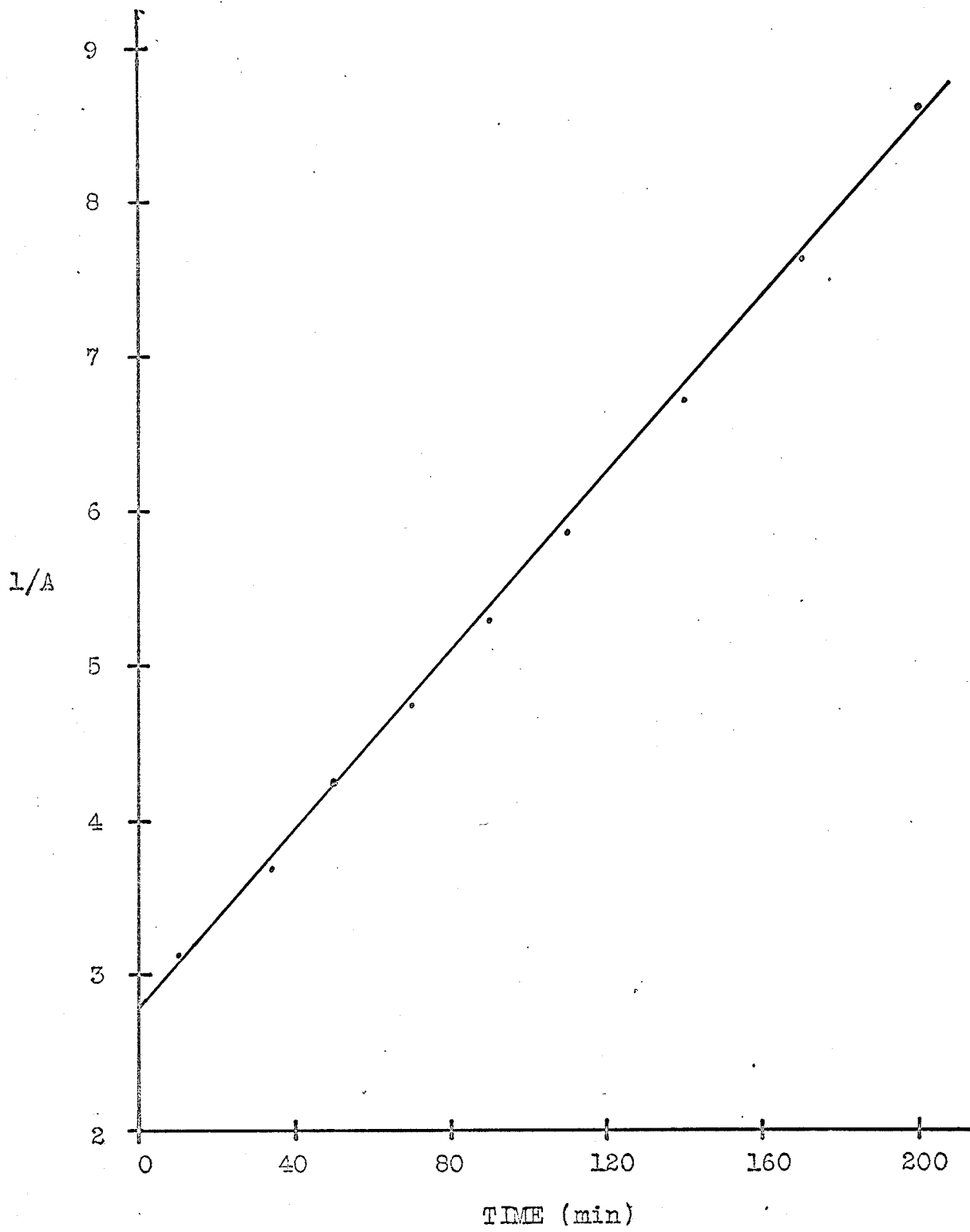


FIGURE 6

TABLE 4

BROMINATION OF MESITYLENE IN ACETIC ACID
IN THE PRESENCE OF PYRIDINIUM CHLORIDE (0.099 M)

$t = 25.0^{\circ}\text{C}$

Initial concentrations: mesitylene 0.0479 M
bromine 0.00115 M

<u>Time (min)</u>	<u>Absorbance</u>	<u>1/Absorbance</u>
0.5	0.220	4.55
1.0	0.192	5.21
1.5	0.174	5.75
2.0	0.157	6.37
2.5	0.142	7.04
3.0	0.131	7.63
3.5	0.121	8.26
4.0	0.111	9.01
4.5	0.102	9.80

FIGURE 7

Figure 7 (a plot of the data of Table 4) gives a plot of $1/A$ versus time for the bromination of mesitylene in acetic acid in the presence of pyridinium chloride (0.099 M).

Initial concentrations: mesitylene 0.0479 M
bromine 0.00115 M

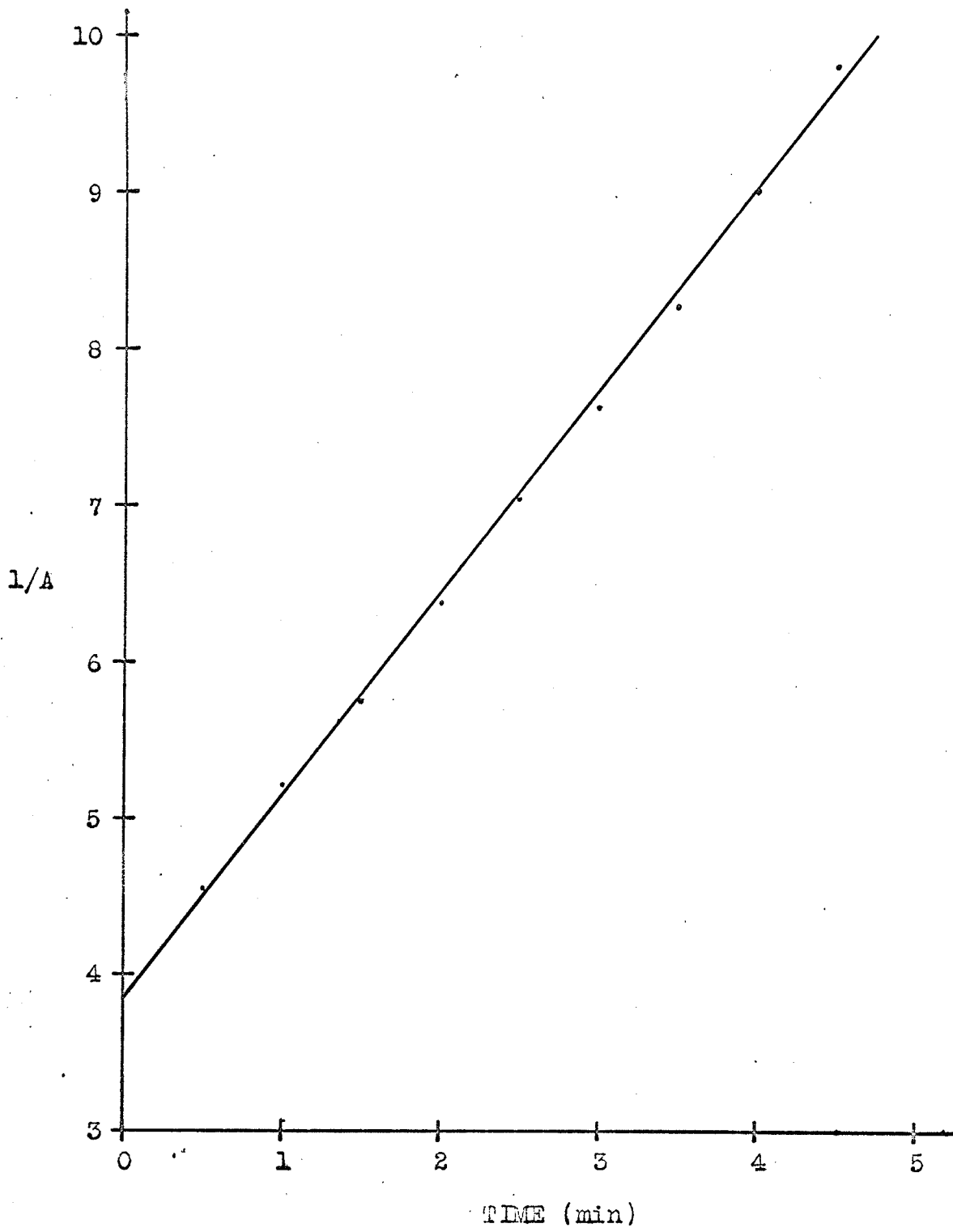


FIGURE 7

TABLE 5

BROMINATION OF MESITYLENE IN ACETIC ACID AT 25.0°C

<u>Mesitylene Conc. x 10² (mole/l)</u>	<u>Bromine Conc. x 10² (mole/l)</u>	<u>Salt Added</u>	<u>Salt Conc. x 10² (mole/l)</u>	<u>k₃ (l²/mole²-min)</u>
4.79	0.205	none		1 x 10 ²
4.79	0.115	C ₅ H ₅ NHCl	9.9	6 x 10 ³
4.74	0.110	¹ TBACl	10.1	2 x 10 ³
4.80	0.110	² NEPCl	10.0	6 x 10 ³

¹TBACl = tetrabutylammonium chloride

²NEPCl = N-ethylpiperidinium chloride

chloride seemed to be the logical choice because it dissolved amine salts satisfactorily and was sufficiently transparent in the ultraviolet spectral region for spectrophotometric determination of equilibrium constants. The majority of the work in ethylene chloride was oriented towards the determination of equilibrium constants between pyridine or pyridinium bromide and bromine. The equilibrium constants were required in order to have a knowledge of how much bromine was complexed and how much was free. It was hoped that this knowledge would be of benefit in planning and interpreting the kinetic studies in this solvent.

Attempts to determine an equilibrium constant for complex formation between bromine and pyridine were discontinued because the spectra of the solutions varied rapidly with time.

Attempts were then made to determine the equilibrium constant between pyridinium bromide and bromine. In this case the spectra of the solutions remained constant with time. However, calculations from the data obtained gave meaningless results. A lengthy investigation into this finally disclosed the source of trouble. It was found that the same concentration of pyridinium bromide in ethylene chloride had markedly different absorbances at 275 millimicrons depending on the method of purification of the solvent and the time since purification. Presumably some decomposition product of ethylene chloride affects the absorbance. Although it had been found earlier that spectra

of solutions of bromine in ethylene chloride remained fairly constant with time, it was found that a solution of bromine in ethylene chloride which had just been purified was very unstable. In this case the absorbance at 275 millimicrons was found to increase from 0.61 to 0.67 in approximately 3 hours. Apparently something forms in ethylene chloride which complexes with bromine thereby increasing the absorbance. It seems that after some time the change in the solvent no longer takes place or the change no longer affects the absorbance after a certain concentration of decomposition product has been reached. One or more decomposition products which affect the absorbance of bromine and pyridinium bromide could influence the amount of complex formed between pyridinium bromide and bromine or affect the absorbance of the complex, thereby accounting for the meaningless results obtained. Work in ethylene chloride was terminated at this point. Subsequently other workers have had trouble with this solvent (75).

5. Studies in Chloroform

After the fruitless endeavours in ethylene chloride, attention was turned to chloroform in continuing the effort to obtain results in an aprotic medium of low polarity. Whereas the instability of ethylene chloride is not well known, the instability of chloroform is well documented (9, 26, 72). In fact, commercial chloroform is sold with ethanol in it as a stabilizer. This ethanol had to be removed before the chloroform

could be used for experimental purposes as ethanol complexes bromine, is liable to be brominated and would affect the polarity of the medium thereby altering the rate. Once the ethanol is removed the chloroform is quite unstable and must be used while fresh. Solutions in pure chloroform must be made up in diffuse light and used immediately. Fortunately, once chloroform starts to decompose, the results are very obviously erratic and that particular work can be abandoned without further waste of time.

a) Equilibrium Constant Determinations

Chloroform solutions of bromine and of pyridinium bromide separately were found to be quite stable at 275 millimicrons. Beer's law studies were satisfactory for bromine. Some deviation from Beer's law was noted for pyridinium bromide. This was expected in view of previously reported work (42). Experimental conditions were always chosen in the following work such that this deviation from Beer's law would have a negligible algebraic effect on the results. Four attempts to determine an equilibrium constant between pyridinium bromide and bromine at 275 millimicrons were made. In all cases erratic results were obtained. As a result this work was given up temporarily. Later, an equilibrium constant determination was tried again. To do this work the need for chloroform as free as possible from decomposition products was now realized. Previously the chloroform was usually purified one day and

used the next day. Presumably by the time it was used it would have some contaminants, not in high enough concentration to affect the rate studies, but perhaps enough to catalyze further decomposition of the solvent. A way was now sought for keeping the chloroform free of contaminants until just a few minutes before use. After some experimentation, storage over chromatographic alumina was found to be ideal. The purified chloroform, stored over this, was found to be stable for at least two or three weeks compared to a day or so when not stored over alumina. It would seem that alumina simply adsorbs the decomposition products as fast as they are formed. A few minutes before the chloroform is required, the alumina is stirred up in it for a brief period of time and then filtered out. Having attained a better quality of chloroform, it was decided to seek experimental conditions less likely to cause erratic results. It was observed throughout the project that, in general, the further into the ultraviolet one works the more sensitive are absorbance values to impurities in the solvent. For this reason a wavelength of 360 was chosen instead of the previous value of 275 millimicrons. In the previous work excess bromine was employed. Because it was thought that high bromine concentrations could hasten decomposition, excess pyridinium bromide and very low bromine concentrations were used in the present attempt. It was also thought that the probability of obtaining consistent results would be increased by decreasing the length of time from when the chloroform was

first put in use until when the absorbance reading was taken. This was accomplished by not using the same stock solution for all final samples as had been done previously. This time fresh stock solutions were made immediately before the preparation of each final solution used in obtaining an absorbance value. That is, each final solution was made up completely independently of all other final solutions and the absorbance value was taken immediately. As a result of these innovations a set of consistent results was obtained. In this work the concentrations used were selected bearing in mind the discussion in the Historical Review on determination of equilibrium constants; experimental concentrations were selected such that the equilibrium concentrations of the complex and bromine (the more dilute component) were of the same order of magnitude. The wavelength chosen was one at which the complex absorbs strongly with negligible interference from pyridinium bromide and bromine.

The results were analyzed on the assumption that only a 1 : 1 complex exists. This is in line with nearly all the work in the literature on determination of equilibrium constants between halogens and organic compounds. In some cases the existence of only a 1 : 1 complex was proven, but in many cases it was just assumed. In view of the known stability of the tribromide ion (see Section D of the Historical Review) there can be no doubt about the existence of a 1 : 1 complex in this case. In view of results already presented in Section A of the Method and Results there is a possibility that another

complex may co-exist with the 1 : 1 complex. Experimental methods (10) are available for determining if more than one complex exists in a solution; however all of these are inapplicable in view of the instability of the system being investigated. Even if it were possible to prove a second complex existed in significant concentration it is extremely unlikely that the stoichiometry could be elucidated in such an unstable system. It was felt that, assuming a 1 : 1 complex would yield a satisfactory result as the main aim in determining the equilibrium constant was to get an estimate of the amount of bromine complexed in order to be able to interpret the kinetic data.

As discussed in Section C of the Historical Review the equilibrium constant for a 1 : 1 complex can be evaluated by equation 3.

$$1/K = S_0 B_0 E/D - S_0 - B_0 + D/E \quad (3)$$

where $D = A - E_s S_0 - E_b B_0$

and $E = E_c - E_s - E_b$.

In this case K represents the relationship

$$K = \frac{(C_5H_5NHBr_3)}{(C_5H_5NHBr) (Br_2)} .$$

S_0 is the initial concentration of pyridinium bromide and B_0 the initial concentration of bromine. All concentrations are in moles/litre. A is the measured absorbance of a given solution. E_c , E_s and E_b refer to the absorptivity of complex, pyridinium

bromide and bromine respectively. The experimental conditions and required accuracy of the result were such that $D/E - B_0$ was ignored and equation 5 (derived previously in Section C of the

$$S_0 = ES_0B_0/D - 1/K \quad (5)$$

Historical Review) was used. Therefore a plot of S_0 versus S_0B_0/D should give a straight line of slope E and intercept $-1/K$. The results obtained at 360 millimicrons and a temperature of 25.0°C are shown in Table 6 and plotted in Figure 8. The estimated experimental errors are shown on the graph. The straight line drawn was arrived at by a least squares treatment of the data. The value of K obtained from this least squares treatment, along with its standard deviation is 198 ± 36 litres/mole. The value of E is 1500 ± 39 litres/mole-cm. The value of E_b , obtained by direct measurement on solutions of bromine, is 38.7 and the value of E_s is 0.3 litres/mole-cm. Thus the absorptivity of the complex is 1539 ± 39 litres/mole-cm.

Using the same sort of procedure as to preparation of solutions that yielded successful results above, an equilibrium constant determination was attempted between tetrabutylammonium bromide (to be referred to from now on as TBABr) and bromine. Preliminary investigation indicated that the formation constant was very much greater than that between pyridinium bromide and bromine. This necessitated the use of exceedingly low concentrations. The absorbances of these dilute solutions were found to drift with time at all wavelengths and at various ratios of bromine to TBABr. The absorbance was observed to drift either

TABLE 6

DATA FOR THE DETERMINATION OF THE EQUILIBRIUM CONSTANT FOR
COMPLEX FORMATION BETWEEN PYRIDINIUM BROMIDE AND BROMINE

$t = 25.0^{\circ}\text{C}$
wavelength = 360 millimicrons

$S_{\text{O}} \times 10^2$ (mole/l)	$B_{\text{O}} \times 10^4$ (mole/l)	\underline{A}	\underline{D}	$(S_{\text{O}}B_{\text{O}} \times 10^5)/\underline{D}$
4.19	5.33	0.735	0.701	3.19
3.37	4.92	0.681	0.651	2.54
0.495	5.98	0.432	0.408	0.72
1.02	5.33	0.561	0.537	1.01
2.29	5.04	0.665	0.638	1.81
1.60	6.08	0.735	0.706	1.38

TABLE 7

DATA FOR THE DETERMINATION OF THE EQUILIBRIUM CONSTANT
FOR COMPLEX FORMATION BETWEEN
TETRABUTYLAMMONIUM BROMIDE AND BROMINE

$t = 25.0^{\circ}\text{C}$
wavelength = 360 millimicrons

$S_{\text{O}} \times 10^4$ (mole/l)	$B_{\text{O}} \times 10^4$ (mole/l)	\underline{A}	\underline{D}
4.36	5.01	0.613	0.594
2.20	2.35	0.277	0.268
9.18	9.56	1.283	1.246

FIGURE 8

Figure 8 (a plot of the data of Table 6) gives a plot of S_0 versus S_0B_0/D . This relationship was used for determining the equilibrium constant for complex formation between pyridinium bromide and bromine.

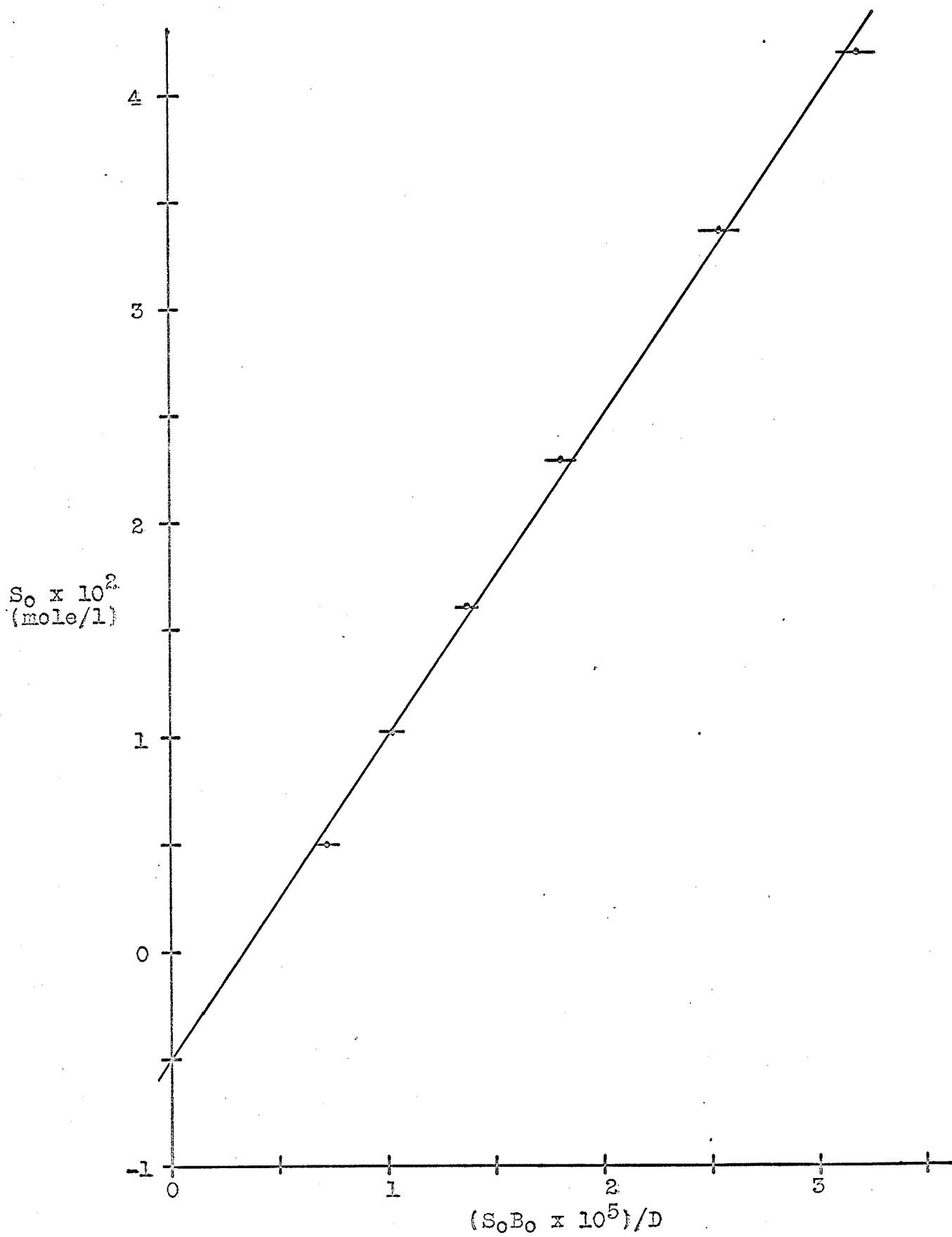


FIGURE 8

up or down depending on the wavelength and concentrations. A probable reason for this instability is that it takes a very low concentration of decomposition product in the chloroform to alter the absorbance of such dilute solutions. The most stable experimental conditions were approximately equal concentrations of TBABr and bromine at 360 millimicrons. Under these conditions the drift in absorbance was never more than 3% in 10 minutes. The initial absorbance reading was always obtained within $2\frac{1}{2}$ minutes of when the TBABr and bromine solutions were mixed. Readings were taken for several minutes in order to estimate back to the reading at the time of mixing. This data, obtained at a temperature of 25.0°C , is given in Table 7.

The results were analyzed by equation 3 (the derivation and use of which is given in Section C of the Historical Review).

$$1/K = S_0 B_0 E/D - S_0 - B_0 + D/E \quad (3)$$

In this case K represents the relationship

$$K = \frac{(\text{TBABr}_3)}{(\text{TBABr}) (\text{Br}_2)}$$

The letters have the meanings given to them above with the exception of S_0 which now refers to the initial concentration of TBABr. The absorptivity of TBABr at this wavelength is negligible. Thus

$$D = A - E_b B_0$$

and
$$E = E_c - E_b.$$

The term $D/E - B_0$ can not be ignored under the conditions employed in this case. The data were analyzed as follows. Each set of data was substituted into the right hand side of equation 3. As there is only one value of l/K these right hand sides of the equation were equated in all possible combinations to solve for E . The value of E obtained is 1490 ± 56 litres/mole-cm. This value of E was put back into the equations to solve for l/K . The value of K obtained is $(9.0 \pm 0.9) \times 10^4$ litres/mole. The absorptivity of the complex is 1529 ± 56 litres/mole-cm, since that of bromine is 38.7 litres/mole-cm.

It is very interesting to note that the absorptivity of both complexes at 360 millimicrons is the same, well within experimental error. This is exactly what is expected if the absorbing complex is the same in both cases. This lends credence to the reliability of the determinations.

b) Rate Studies

Rate studies of brominations in chloroform (35) have been made previously by Josephson, Keefer and Andrews. They found that the bromination of mesitylene was second order in bromine and that nuclear rather than side chain bromination was the predominant process. Their observations as to order and rate were reproduced satisfactorily by the author both with freshly purified chloroform and with chloroform which had been stored over alumina. The runs reported here were followed

spectrophotometrically as were those of the above mentioned authors. Josephson et al. in their study did not include any work with salts.

In all of the work reported here by the author, mesitylene was present in substantial excess. In all cases quoted, the rate measurements were made at a wavelength where bromine and the bromine-salt complex had the same absorptivity (as determined by the isosbestic point) so that the total bromine would have a linear relationship with absorbance. The salts were found to be stable to bromine within experimental error, as the absorbance of solutions containing bromine and salts was found to be stable for the time of the slowest rate runs.

Third-order rate constants were determined by making use of equation 10, which was derived in Section B : 3 of the Method and Results.

$$1/A = k_3Mt/e + 1/ae \quad (10)$$

where $A = eB$.

M, B and a are the concentrations of mesitylene, total bromine and initial total bromine respectively in moles/litre. t is the time and k_3 is the third-order rate constant. A is the absorbance and e is the absorptivity of total bromine. e is determined from the absorbance at zero time and an iodometric determination of the initial bromine concentration. If the reaction is second order in total bromine, a plot of $1/A$ versus t will give a straight line with a slope equal to k_3M/e . k_3 is calculated from this value.

Second-order rate constants were determined as follows. For a second-order reaction of this type, with mesitylene in large excess, the integrated rate expression is

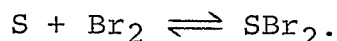
$$-2.3 \log B = k_2 M t - 2.3 \log a.$$

k_2 is the second-order rate constant and the rest of the letters have the same meaning as noted above. On substituting $B = A/E$ and rearranging the following equation is obtained.

$$-\log A = k_2 M t / 2.3 - \log ea$$

If the reaction is first order in total bromine a plot of $-\log A$ versus t will give a straight line with a slope equal to $k_2 M / 2.3$. k_2 is calculated from this value.

It will be noted that the above two derivations give the rate constants on the basis of total bromine. In some cases it is important to have the rate constants on the basis of free bromine. It is highly unlikely that bromination by trihalide ion will be significant (51). Bromine will be complexed by the halide salts according to



Let B and (B_f) be the concentrations of total bromine and free bromine respectively in moles/litre. S refers to the salt in the same concentration units. The salt was always present in constant large excess. Substituting into the equilibrium constant relationship yields

$$K = \frac{B - (B_f)}{S(B_f)} .$$

Rearrangement gives

$$(B_f) = B/(KS + 1).$$

Consider a reaction whose rate has been found experimentally to be represented by

$$-dB/dt = k_2MB.$$

As above, M is the mesitylene concentration in moles/litre and k_2 is the second-order rate constant in terms of total bromine. If free bromine is the substituting agent the rate can equally well be represented by the above form of equation because

$$-dB/dt = (k_2)_f M(B_f) = (k_2)_f MB/(KS + 1)$$

where $(k_2)_f$ is the second-order rate constant in terms of free bromine and K and S are constants with the significance previously stated. It follows that

$$(k_2)_f = k_2(KS + 1).$$

By a similar procedure it can be shown that

$$(k_3)_f = k_3(KS + 1)^2$$

where $(k_3)_f$ is the third-order rate constant in terms of free bromine.

Some of the work in chloroform is summarized in Table 8. Representative data are given in Tables 9 - 13 and representative plots are given in Figures 9 - 13.

The following are observations pertinent to the results obtained. The results with pyridinium bromide (Figure 10) were found to obey a fairly good first-order-in-bromide relationship for as long as the run was followed (greater than

TABLE 8

BROMINATION OF MESITYLENE IN CHLOROFORM AT 25.0°C

<u>Added Salt</u>	<u>none</u>	<u>none</u>	<u>C₅H₅NHBr</u>	<u>C₅H₅NHBr</u>	<u>C₅H₅NHCl</u>	<u>C₅H₅NHCl</u>
Mesitylene Conc. (mole/l)	0.199	0.190	0.189	0.189	0.202	0.20
Initial Bromine Conc. x 10 ³ (mole/l)	4.21	4.96	3.93	4.28	5.21	4.25
Salt Conc. (mole/l)			0.096	0.100	0.101	0.549
Dominant Order in bromine	2nd	2nd	1st	1st	2nd	mixed
Ca. time for 50% reaction (sec)	6060	6000	16000	18000	2000	1640
k_3 (l ² /mole ² -sec)	0.187	0.175			0.455	
$k_2 \times 10^4$ (l/mole-sec)			2.32	2.09		
$(k_2)_f \times 10^3$ (l/mole-sec)			4.66	4.34		

TABLE 9
RATE DATA FOR THE BROMINATION
OF MESITYLENE IN CHLOROFORM AT 25.0°C

Initial concentrations: mesitylene 0.199 M
bromine 0.00421 M

<u>Time (sec)</u>	<u>Absorbance</u>	<u>1/Absorbance</u>
52	0.736	1.359
105	0.727	1.376
169	0.721	1.387
371	0.687	1.456
605	0.671	1.490
1000	0.636	1.572
1421	0.602	1.661
1762	0.579	1.727
2131	0.557	1.795
2564	0.530	1.887
2945	0.507	1.972
3545	0.476	2.10
4037	0.456	2.19
4692	0.427	2.34
5270	0.405	2.47
6063	0.376	2.66
6887	0.348	2.87
7520	0.325	3.08
8286	0.307	3.26
9265	0.282	3.55

FIGURE 9

Figure 9 (corresponds to the data of Table 9) gives a plot of $1/A$ versus time for the bromination of mesitylene in chloroform in the absence of added salts.

Initial concentrations: mesitylene 0.199 M
bromine 0.00421 M

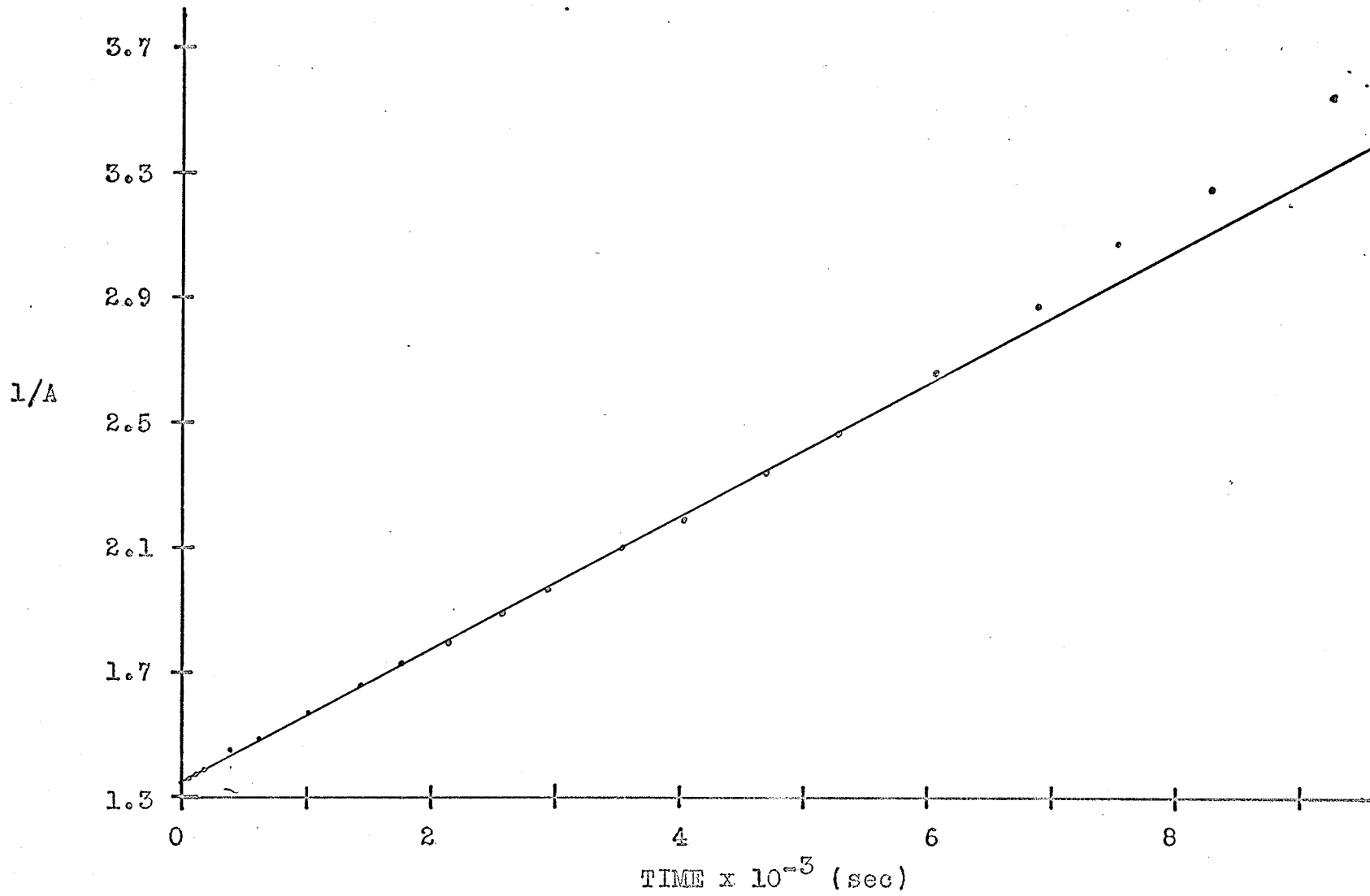


FIGURE 9

TABLE 10

RATE DATA FOR THE BROMINATION OF MESITYLENE IN CHLOROFORM
AT 25.0°C IN THE PRESENCE OF PYRIDINIUM BROMIDE (0.096 M)

Initial concentrations: mesitylene 0.189 M
bromine 0.00393 M

<u>Time (sec)</u>	<u>Absorbance</u>	<u>- log Absorbance</u>
67	0.704	0.152
545	0.683	0.166
965	0.668	0.175
1285	0.663	0.179
1891	0.645	0.190
2444	0.634	0.198
3035	0.619	0.208
3695	0.605	0.218
4688	0.584	0.234
5873	0.554	0.257
6495	0.543	0.265
7475	0.518	0.286
9172	0.478	0.321
10498	0.449	0.348
11915	0.423	0.374
13568	0.389	0.410
14755	0.372	0.430
16215	0.344	0.463
17930	0.319	0.496
20468	0.289	0.539
23076	0.254	0.595

FIGURE 10

Figure 10 (corresponds to the data of Table 10) gives a plot of $-\log A$ versus time for the bromination of mesitylene in chloroform in the presence of pyridinium bromide (0.096 M).

Initial concentrations: mesitylene 0.189 M
bromine 0.00393 M

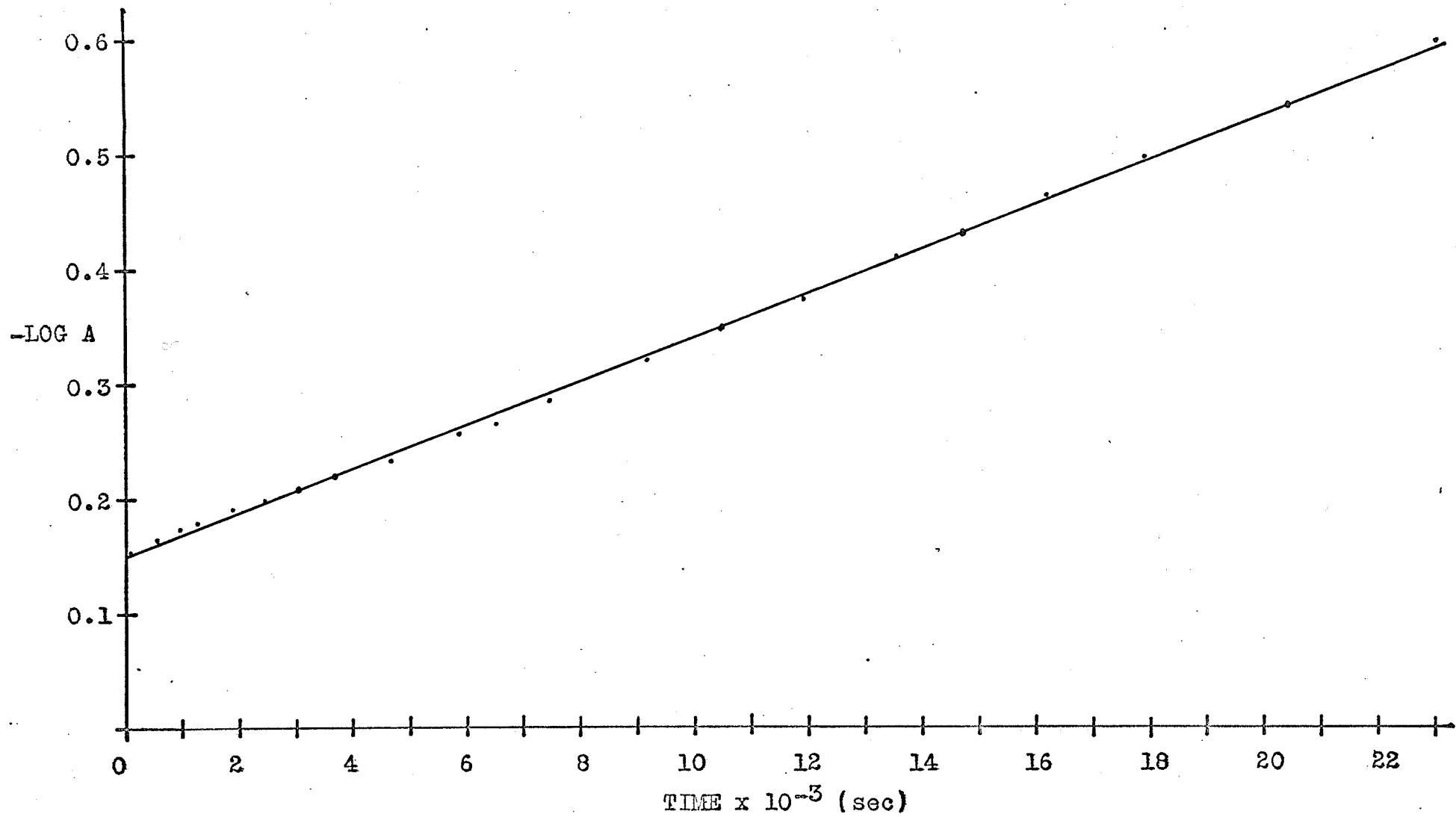


FIGURE 10

TABLE 11

RATE DATA FOR THE BROMINATION OF MESITYLENE IN CHLOROFORM
 AT 25.0°C IN THE PRESENCE OF PYRIDINIUM CHLORIDE (0.101 M)

Initial concentrations: mesitylene 0.202 M
 bromine 0.00521 M

<u>Time (sec)</u>	<u>Absorbance</u>	<u>1/Absorbance</u>
70	0.908	1.10
180	0.852	1.17
272	0.810	1.24
378	0.770	1.30
488	0.733	1.36
645	0.692	1.45
832	0.644	1.55
1089	0.597	1.68
1319	0.558	1.79
1571	0.522	1.92
1878	0.483	2.07
2307	0.441	2.27
2844	0.394	2.54
3327	0.359	2.79
4033	0.319	3.14
5201	0.264	3.79
6122	0.231	4.33
6965	0.205	4.88
8353	0.171	5.85

FIGURE 11

Figure 11 (corresponds to the data of Table 11) gives a plot of $1/A$ versus time for the bromination of mesitylene in chloroform in the presence of pyridinium chloride (0.101 M).

Initial concentrations: mesitylene 0.202 M
bromine 0.00521 M

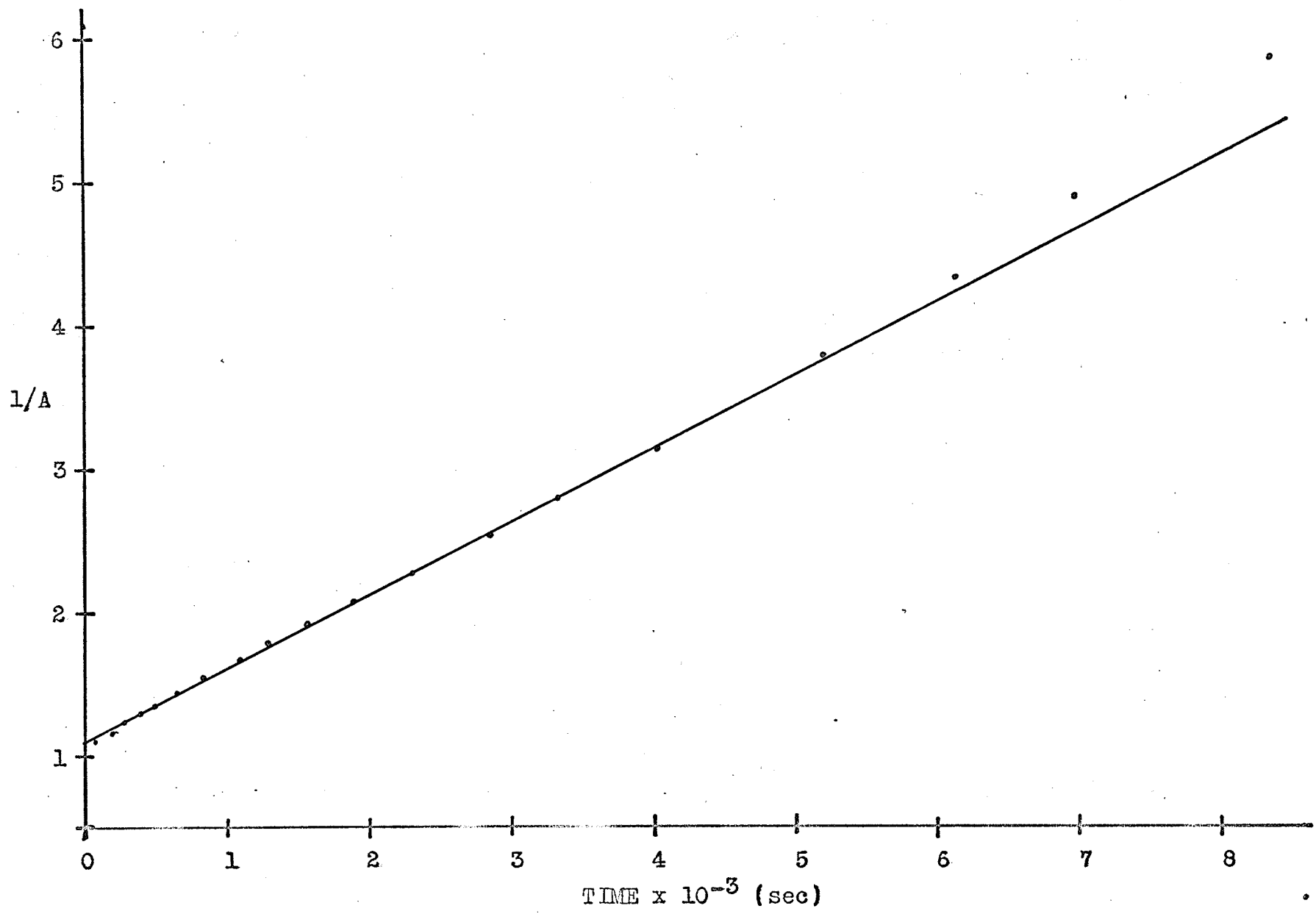


FIGURE 11

TABLE 12

RATE DATA FOR THE BROMINATION OF MESITYLENE IN CHLOROFORM
AT 25.0°C IN THE PRESENCE OF PYRIDINIUM CHLORIDE (0.549 M)

Initial concentrations: mesitylene 0.20 M
bromine 0.00425 M

<u>Time (sec)</u>	<u>Absorbance</u>	<u>- log Absorbance</u>	<u>1/Absorbance</u>
67	0.518	0.286	1.93
131	0.503	0.298	1.99
250	0.477	0.322	2.10
390	0.449	0.348	2.23
594	0.413	0.384	2.42
822	0.374	0.427	2.67
1154	0.324	0.490	3.09
1492	0.283	0.548	3.53
1790	0.251	0.600	3.98
2128	0.219	0.660	4.57
2485	0.192	0.717	5.21
2895	0.164	0.785	6.10
3403	0.136	0.867	7.35
4135	0.104	0.983	9.62
5012	0.0755	1.122	13.33

FIGURE 12

Figure 12 (corresponds to the data of Table 12) gives plots of $1/A$ versus time and $-\log A$ versus time for the bromination of mesitylene in chloroform in the presence of pyridinium chloride (0.549 M).

Initial concentrations: mesitylene 0.20 M
bromine 0.00425 M

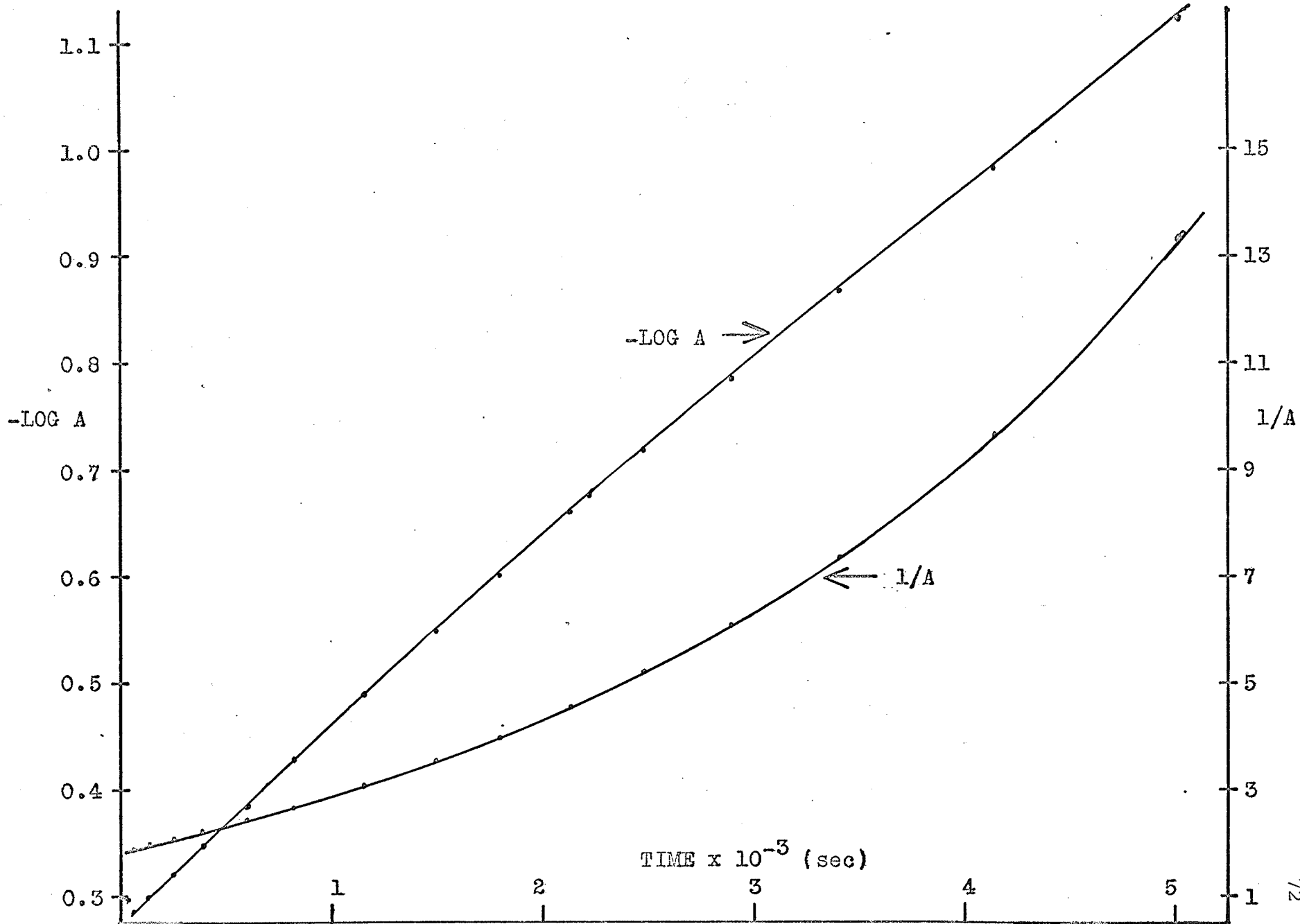


FIGURE 12

TABLE 13

RATE DATA FOR THE BROMINATION
OF MESITYLENE IN CHLOROFORM AT 25.0°C IN THE
PRESENCE OF TETRABUTYLAMMONIUM PERCHLORATE (0.100 M)

Initial concentrations: mesitylene 0.0602 M
bromine 0.004 M

<u>Time (min)</u>	<u>Absorbance</u>
0	0.658
1.0	0.523
2.0	0.465
3.0	0.432
4.0	0.410
5.0	0.395
6.0	0.385
8.0	0.370
10.0	0.359
12.0	0.351
18.0	0.336
31.0	0.320
60.0	0.307
101.0	0.290

FIGURE 13

Figure 13 (corresponds to the data of Table 13) gives a plot of A versus time for the bromination of mesitylene in chloroform in the presence of tetrabutylammonium perchlorate (0.100 M).

Initial concentrations: mesitylene 0.0602 M
bromine 0.004 M

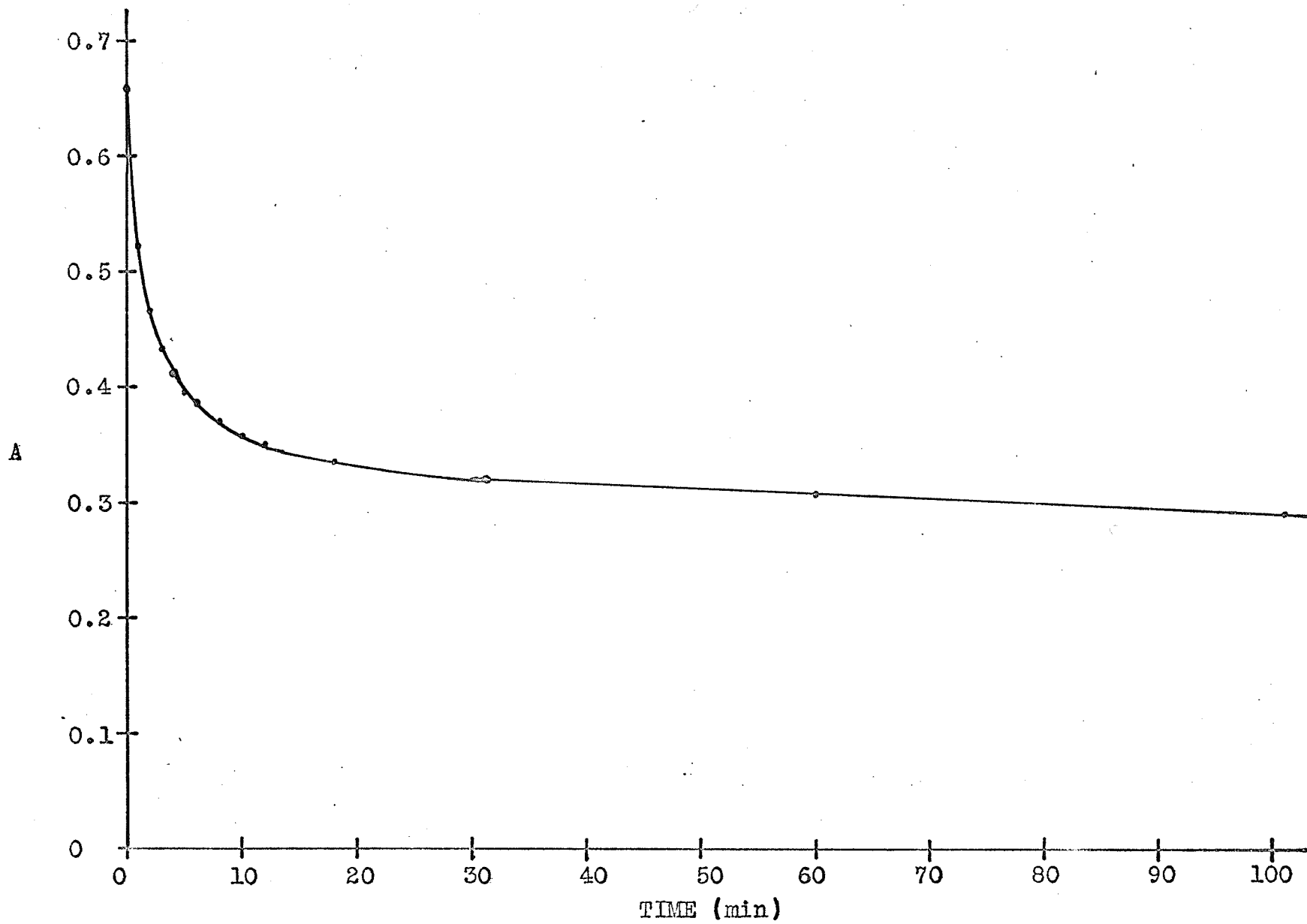


FIGURE 13

70% reaction). However, it should be noted that in view of the not-quite-perfect fit of the straight line plot there is a distinct possibility that a significant contribution from a second-order-in-bromine reaction might be present. With 0.1 M pyridinium chloride (Figure 11) the second-order-in-bromine relationship was obeyed for 70% of the reaction, after which there was deviation. The data for 0.55 M pyridinium chloride was plotted as both first and second order in bromine (Figure 12). It was clearly evident from these plots that the reaction was mixed first and second order in bromine. The reaction was followed to 85% of completion. The remainder of the results did not lend themselves to tabulation and are presented here. In the presence of TBABr (0.101 M), the mesitylene (0.187 M) consumed less than 3% of the bromine (0.00561 M) in two hours. The rate of the reaction was too slow to attempt to determine the order. A reaction in the presence of tetrabutylammonium perchlorate (0.100 M) was very unusual (Figure 13). Mesitylene (0.0602 M) consumed bromine (ca. 0.004 M) very rapidly at first and then the later stages of the reaction were extremely slow. Minor deviations from Beer's law could be present in this case because of the formation of $TBABr_3$. The deviation will not be very great as previous experimental work showed that tribromide ion has approximately the same absorptivity as bromine at the wavelength employed (444 millimicrons). Inspection of Figure 13 suggests that, perhaps, the first 20% of this reaction proceeds without serious interference from

reaction products. Assuming that the order is one with respect to bromine an estimate of k_2 for the first 20% reaction can be obtained as follows. From above

$$-\log A = k_2 Mt / 2.3 - \log e_a.$$

Substituting $e_a = A_0$ (where A_0 is the initial absorbance) and rearranging yields

$$\log (A_0/A) = k_2 Mt / 2.3.$$

The resulting estimate of k_2 is 6×10^{-2} litres/mole-sec.

An explanation of these results is presented in the Discussion of Results.

6. Bromination in Carbon Tetrachloride

As a result of the claim by Yeddanapalli and Gnanapragasam (76) that pyridine was a catalyst in carbon tetrachloride, this work was re-investigated. In their work a bromine concentration of 0.02 M and pyridine concentrations of 0.002, 0.02 and 0.2 M were used. It was found in this laboratory that, at a concentration of 0.01 M pyridine a complex of bromine and pyridine or, much more likely, pyridinium bromide precipitated almost immediately after the reaction started. It is possible that they did not notice the precipitate because of the manner in which they performed the runs. They did not withdraw aliquots but used separate solutions for each analysis. Presumably they stopped the reactions by adding potassium iodide solution before withdrawing the flask containing the sample from the thermostat. These findings on solubility are supported by

Williams (74) who reported that a saturated solution of pyridine dibromide in carbon tetrachloride is about 0.02 M. It has been noted in this project that pyridinium tribromide is much less soluble than pyridine dibromide in solvents of low polarity and thus would be expected to precipitate as the reaction proceeded. It is quite possible that the catalysis noticed by Yeddanapalli and Gnanapragasam was a surface effect and not one in a homogeneous medium.

IV. DISCUSSION OF RESULTS

A. DISCUSSION OF RESULTS IN CONCENTRATED BROMINE SOLUTIONS

Prior to discussing the effect of pyridine on bromination, the complexes isolated in this work will be considered. As shown in Section A of the Method and Results, II has a molecular composition represented by $(C_5H_5NHBr)_3(Br_2)_2$. It is possible that the bromine could be complexed with the bromide ion and/or with the pyridinium cation. Though there is experimental evidence (42) that the pyridinium cation has sufficient electrophilic character (through its pi electron system) to form a weak complex with the iodide ion, it is highly unlikely that this cation would have a significant interaction of this type with the bromine molecule which is far less nucleophilic than the iodide ion. Bromine has only a weak interaction with pi donors such as aromatic molecules (37) in comparison to the much greater interaction of bromine with bromide ion to form the stable tribromide ion (Section D of the Historical Review). In view of this information a more appropriate way of representing the molecular composition would seem to be $(C_5H_5NHBr_3)_2C_5H_5NHBr$. If this interpretation is correct, II must crystallize, for reasons of stability within the crystal structure, with two molecules of pyridinium tribromide for every molecule of pyridinium bromide. However, it should be noted that the existence of such a stoichiometry in the solid state is not proof that it exists in solution.

As expressed in Section A of the Method and Results, there can be no doubt that every molecule of pyridine in II is protonated. Complex I is much less stable and harder to analyze, but it seems reasonable to assume that the pyridine in this complex is also protonated. The following is offered to justify this assumption. It should be recalled that I precipitates when pyridine is added to an approximately equimolar mixture of benzene and bromine at room temperature. The amount of pyridine added was 1 to 2%, on a molar basis, of the amount of bromine used. Under these experimental conditions there would be sufficient hydrogen bromide to protonate the pyridine after only about 2% of the benzene is brominated. The relative solubilities of protonated and deprotonated bromine-pyridine complexes favour the formation of a protonated species. It was noted in this project that the protonated complexes were less soluble in solvents of low polarity. In particular, as is noted in Section A of the Method and Results, passing anhydrous hydrogen chloride into a solution of $C_5H_5NBr_2$ in ethylene chloride precipitated a complex containing both bromine and hydrogen chloride. Further evidence for the protonation of I is that I and II appear to be formed reversibly from one another. As described in Section A of the Method and Results, I converts into II on standing at room temperature. Also described in that section is the conversion of II, on being placed in a benzene-bromine (mole ratio ca. 1 : 1) solution at room temperature, to a material having all the characteristics

of I. If II, which is protonated, causes precipitation of I on being placed in a bromine solution of high concentration, then I should also be protonated. I could be non-protonated if such a form were less soluble but, as pointed out above, the evidence indicates that protonated bromine-pyridine complexes are less soluble.

A $\text{Br}_2 : \text{C}_5\text{H}_5\text{NHBr}$ ratio of 2 : 1 requires 68% reducible bromine and a ratio of 3 : 1 requires 75% reducible bromine. The experimental value of 70% favours the 2 : 1 ratio. The high value obtained could easily be accounted for by the bromine occluded to the solid. As mentioned in Section A of the Method and Results, washing of I was not possible because of its instability. Taking all these considerations into account the most reasonable stoichiometry for I would seem to be $\text{C}_5\text{H}_5\text{NHBr}(\text{Br}_2)_2$. Whether this should be written $\text{C}_5\text{H}_5\text{NH}^+\text{Br}_5^-$ or whether part of the reducible bromine is associated with the pyridinium cation can not be decided from the information presently available. However, whether or not part of the bromine is associated with the cation is not important to the discussion that follows.

In the re-investigation of Cohen's work it was found that pyridine does increase the rate of bromination, but accurate quantitative data were not obtained because of the heterogeneity of the system. Consequently, nothing definite can be concluded about the mechanism.

In addition to added pyridine catalyzing the reaction it was noted (Section A of the Method and Results) that addition of some of I to a mixture of benzene and bromine in the Cohen concentrations at room temperature produced an increase in the rate of bromination. Also, filtration of I from the mixture caused a decrease in the rate of bromination. This suggests it is not any species in solution which is causing the catalysis, but that it must be a surface effect.

On increasing the temperature of the reaction mixture from room temperature to ca. 35°C the solid no longer exists. In its place is a small second liquid layer at the bottom of the flask. The fact that both layers were the same dark color indicates they both contain large concentrations of bromine. The very existence of this small second layer suggests that it must be significantly more polar than the 'benzene' layer, otherwise it would not form. If such is the case, this small second layer must owe its polarity (and existence) to the pyridinium bromide (or bromine complexes thereof) formed in the course of the reaction.

As a result of the complicated system involved, it is difficult to draw any definite conclusions from this work. However, consideration of these results in concentrated bromine solution can be facilitated by taking into account the work in dilute bromine solutions. The results in dilute bromine solution will be discussed in Section B of the Discussion of

Results; just the pertinent conclusions of that discussion are quoted here. (a) The results indicate that $C_5H_5NBr_2$, the molecular complex of pyridine and bromine, is a poorer brominating agent than bromine, if it brominates at all. (b) Pyridinium bromide and TBABr decreased the rate of bromination. This is believed to be caused by complexing of bromine by bromide ion to form tribromide ion which is a much poorer brominating agent than bromine. (c) Bromination has been shown to be accelerated by pyridinium chloride and other amine salts. This indicates there is nothing unique about the ability of a pyridinium salt to increase the rate. The results were accounted for on the basis of a polarity effect rather than a specific intervention of the salt in the transition state of the rate-determining step.

If these conclusions can be applied to the work in concentrated bromine solutions, it can be postulated that the increase in rate is because of a polarity effect and not because of specific intervention by pyridine, pyridinium bromide or some complex thereof in the transition state of the rate-determining step. As suggested above, the small second layer should be significantly more polar than the 'benzene' layer. The surface of complex I (which exists instead of the small second liquid layer at slightly lower temperature) is also probably more polar than the 'benzene' layer. Pyridinium bromide would not be expected to retard the rate in the work

involving concentrated bromine solutions because the bromine is in such great excess that neither pyridine nor its salts could tie up a significant fraction of it.

As noted in Section A:1 of the Method and Results, the results of the brominations (employing concentrated bromine solutions) of tert-butylbenzene in the presence of pyridine and different amine salts will be of questionable validity because of the existence of two liquid layers. However, it is interesting that the results obtained are consistent with the above postulate. Each of pyridine, pyridinium chloride, pyridinium bromide and TBABr increased the rate by a similar amount. This, of course, implies that essentially all of the pyridine is protonated in order to have an analagous salt effect.

The same considerations apply to the work of de la Mare and Harvey (19) and the work of Cross and Cohen (17), referred to in Section A of the Historical Review, wherein pyridine is employed as a catalyst in concentrated bromine solutions.

B. DISCUSSION OF RESULTS IN DILUTE BROMINE SOLUTIONS

1. Introduction

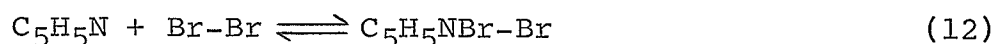
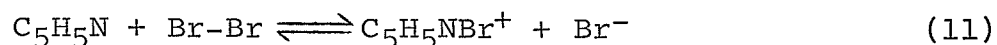
As was shown in Sections B:1 and B:2 of the Method and Results, the rates of bromination of both o-nitroanisole in aqueous solution and of pure benzene were decreased on addition

of pyridine. This indicates that $C_5H_5NBr_2$, the molecular complex of pyridine and bromine (74), is a poorer brominating agent than bromine, if it brominates at all. It is realized that this is in contradiction to most of the hypotheses referred to in Section A of the Historical Review. As described there, chemists have suggested that the product of the reaction of a halogen and pyridine could be a more ready source of positive halogen than the halogen molecule itself. Compounds such as $C_5H_5NBr^+Br^-$ seem to have been envisioned.

The viewpoint of the author is as follows. First, consider the discussion of mechanism in aromatic bromination presented in Section B of the Historical Review. It will be recalled that the currently accepted mechanism for the un-catalyzed reaction, and for the reaction catalyzed by weak electrophiles such as iodine, involves a rate-determining heterolysis of the bromine-bromine bond in the $ArHBr_2$ complex. Evidence has also been presented that the rate of the heterolysis step can be greatly increased by an increase in the polarity of the medium, caused by addition of water or salts to the solvent. It was also pointed out in that section that strong electrophiles such as ferric chloride are capable of altering the mechanism of the un-catalyzed reaction by making the halogen sufficiently electrophilic that heterolysis of the bromine-bromine bond is no longer kinetically important and that the over-all rate is much faster. It should also be recalled to mind that both the

catalyzed and uncatalyzed brominations do not exhibit a kinetic hydrogen-isotope effect with the exception of a few very reactive or very sterically hindered aromatic compounds. It follows that there are two ways (excluding the creation of a more polar medium) by which a compound can increase the rate of reaction: (a) by assisting in the heterolysis of the bromine-bromine bond of the ArHBr_2 complex by direct intervention in this step or (b) by increasing the electrophilic character of the attacking bromine sufficiently that heterolysis of the bromine-bromine bond is no longer kinetically important.

Pyridine, being essentially a nucleophile, can not act in the former role as this requires an electrophile. The possibility of pyridine acting in the latter role can not be decided so easily. The two extreme possibilities in the nucleophilic attack on bromine by pyridine can be represented by the following two equations.



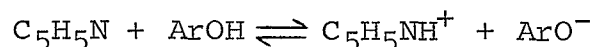
When bromine and pyridine interact in equation 11, the product (to be referred to as structure A) is ionized, whereas in equation 12 the product (to be referred to as structure B) is a covalent structure necessitating expansion of the bromine octet. Equation 11 is what other authors seem to have in mind when they suggest that the product of the reaction of a halogen and pyridine could be a more ready source of positive halogen

than the halogen molecule. It is to be expected that the bromine atom bonded to nitrogen in A would be more electrophilic than the bromine molecule. The bromine in B would be expected to be less electrophilic than the bromine molecule because it has two more valence electrons than a bromine molecule.

It would be difficult to predict a priori whether the true structure would more closely resemble A or B. It is to be expected that the resulting structure would be influenced by the solvent employed and which halogen is being used. The experimental results obtained in this study indicate that the product obtained with bromine and pyridine in both water and benzene resembles structure B sufficiently that it is less electrophilic than the bromine molecule, thereby retarding the reaction. In agreement with this interpretation Yeddanapalli and Gnanapragasam (76) attributed retardation with excess pyridine to a decrease in the concentration of free bromine due to formation of $C_5H_5NBr_2$. They offered no explanation for why this complex should be a poorer brominating agent than bromine.

The work (56) of Pershina and Borodina (mentioned in Section A of the Historical Review), which showed that pyridine facilitated the iodination of phenols, can be explained in at least three different ways. Perhaps for iodine the product obtained with pyridine resembles structure A sufficiently that it is more electrophilic than molecular iodine, thereby

accelerating the reaction. Secondly, a possible explanation is that, for the reactions they studied, proton loss from the ArHI^+ complex was the rate-determining step and pyridine was catalyzing by assisting in the departure of the proton. Rate-determining proton loss has been observed for some aromatic iodinations (29). Thirdly, the catalysis could be caused by



since ArO^- will be more reactive than ArOH (32).

Of the remaining examples of catalysis referred to in Section A of the Historical Review, the publication of Yeddanapalli and Gnanapragasam (76) will be discussed later. Sufficient information about the work of Tronov and Loginova (68) is not available to make a discussion of this possible.

2. Bromination in Acetic Acid

As shown in Table 5 of the Method and Results, pyridinium chloride, tetrabutylammonium chloride and N-ethylpiperidinium chloride all caused notable increases in the rate of bromination of mesitylene in acetic acid. As noted in that section, the third-order reaction provides the major portion of the over-all bromination for both the catalyzed and the un-catalyzed reactions. In view of the mechanism of the third-order reaction in which the rate-determining heterolysis of the bromine-bromine bond of the ArHBr_2 complex is thought to be assisted by a second bromine molecule, it would seem reasonable to ascribe the increase in rate to a change in solvent polarity as it is unlikely that two

species could be directly assisting in the heterolysis. It follows that the main cause of the increase in rate must be the change in solvent polarity. Keefer, Ottenberg and Andrews (39) found significant, but smaller, increases in the third-order bromination reaction in acetic acid on adding salts of the alkali metals (lithium chloride, lithium perchlorate, sodium acetate and sodium perchlorate). They also attributed the increase in the rate constant to a change in solvent polarity.

The work in this study points out that there is nothing unique about the ability of a pyridinium salt to increase the rate as the same increase in rate was observed for N-ethylpiperidinium chloride. The increase in rate caused by tetrabutylammonium chloride is not quite as great. A possible explanation for this is that more of the bromine may be complexed in the tetrabutylammonium chloride work. As observed in this study (Section B:5:a of the Method and Results), TBABr forms a very much stronger complex with bromine than does pyridinium bromide. Similarly it is to be expected that TBACl will form a stronger complex with bromine than will pyridinium chloride. It is well known that Br_3^- is a poorer brominating agent than Br_2 (51). By analogy it is to be expected that Br_2Cl^- will be a poorer brominating agent than Br_2 . Thus the retarding effect due to formation of a greater amount of Br_2Cl^- will partially counteract the acceleration due to the increase in solvent polarity.

The three substituted ammonium chlorides all accelerated the rate of bromination; however, as described in Section B:3 of the Method and Results, pyridinium bromide strongly retards the rate of bromination. As mentioned above, there are two opposing factors to be considered: (a) retardation caused by the formation of a trihalide salt and (b) acceleration caused by an increase in solvent polarity. It is to be expected that pyridinium bromide would have a similar effect on the solvent polarity to that of the above chlorides. The formation constant for the tribromide ion must be significantly greater than that for the dibromochloride ion, thereby accounting for retardation in the former case and acceleration in the latter case. The formation constant for the dibromochloride ion in acetic acid is not available, but the formation constants in water support the above view. It has been noted previously that an inorganic chloride (39) increases the rate of bromination and that an inorganic bromide (77) decreases the rate of bromination.

As discussed in Section B:3 of the Method and Results (and shown graphically in Figure 5) the presence of pyridine accelerates bromination in acetic acid. However, it was noted that the smallest amount of pyridine caused the greatest amount of acceleration and the largest amount of pyridine caused the least acceleration. A possible explanation for this follows. Pure acetic acid is believed to exist in a dimeric form due to hydrogen bonding. The presence of pyridine would certainly

be expected to create a more polar medium as there would be a greater tendency for pyridine to hydrogen bond with acetic acid (if not actually form pyridinium acetate) than there would be for two acetic acid molecules to hydrogen bond. Pyridine, either protonated or hydrogen bonded to acetic acid, would surely increase the polarity over that of acetic acid dimers. The pyridine also reacts with the bromine present to form $C_5H_5NBr_2$ (which we can assume, from the work in benzene and water, does not brominate at all or is not as good a brominating agent as molecular bromine). The rate of reaction will be determined by two opposing factors: (a) retardation caused by formation of $C_5H_5NBr_2$ and (b) acceleration caused by an increase in solvent polarity. In order to account for the increase in rate caused by pyridine one must suppose that small concentrations of pyridine increase the rate by altering the polarity of the medium more than they retard by formation of $C_5H_5NBr_2$. Increasing the pyridine concentration ties up more and more bromine so that the resulting decrease in rate offsets the increases caused by solvent polarity. All of the runs had pyridine concentrations such that the initial rate was greater than with no pyridine added.

3. Complex Formation in Chloroform

Under the conditions employed in this study, it would seem quite certain that the major complex between TBABr and bromine in chloroform is that containing the tribromide ion.

The only other possibility for this complex is that resulting from the formation of pentabromide ion. This species is known to exist but its stability has been reported (64) to be considerably less than that of the tribromide ion. When bromine is present in very large excess (as, for example, in the Cohen conditions) it is quite likely that pentabromide ion might be found. Taking into account the instability of the pentabromide ion, it would seem that this species could not be present in significant amount in this study where bromine was either in equimolar concentration with the bromide or as the minor constituent.

Similarly, it is to be expected that the major complex between pyridinium bromide and bromine in chloroform is that of the tribromide ion. This can be justified as follows. Any significant contribution from the pentabromide ion can be ruled out as in the above case. It is known that bromine has only a weak interaction with pi donors of the aromatic type (37). Though there is experimental evidence (42) that the pyridinium cation has sufficient electrophilic character (through its pi electron system) to form a weak complex with the iodide ion, it is highly unlikely that this cation would have a significant interaction of this type with the bromine molecule which is far less nucleophilic than the iodide ion. In view of this information and the well known stability of the tribromide ion (see Section D of the Historical Review) it seems likely that the

tribromide complex will be the only one of these existing in significant concentration.

As mentioned earlier in the Discussion of Results a stable complex of the stoichiometry $(C_5H_5NHBr_3)_2C_5H_5NHBr$ has been isolated. It is impossible to conceive of any regular sigma type bonding which would hold this species together. Therefore it must be assumed that geometrical factors, pi bonding and Coulombic forces (which in this case might include any or all of hydrogen bonding, van der Waals, dipole-dipole, ion-dipole, dipole-induced dipole forces) are sufficient to cause two molecules of pyridinium tribromide to crystallize with one molecule of pyridinium bromide in forming a stable solid. However, it would seem probable that these forces will be insufficient to preserve this entity in solution in more than very minimal amounts in comparison to the concentration of pyridinium tribromide.

That the complex between TBABr and bromine and the complex between pyridinium bromide and bromine contain the same absorbing entity (this entity would be tribromide ion according to the above argument) is supported by the fact that both complexes were found to have the same absorptivity at 360 millimicrons within experimental error. Although the author is confident that the major complex in both of the above cases (and in the kinetic studies where added bromide was used) is that containing the tribromide ion, it should be pointed out

that a knowledge of the structure of the complex is not necessary for interpretation of the kinetic results as long as the structure is such as to make it a decidedly less active brominating agent than bromine. All that is required is a knowledge of the amount of bromine tied up as complex.

The value of 9×10^4 litres/mole for the formation constant of the TBABr-bromine complex is surprisingly large in comparison to the value of 198 litres/mole for the formation constant of the pyridinium bromide-bromine complex. However, this is perfectly compatible with the rate studies in chloroform for here it was found that in the presence of 0.1 M TBABr, mesitylene (0.187 M) consumed less than 3% of the bromine (0.00561 M) in two hours, whereas in the presence of the same concentration of pyridinium bromide, reaction proceeded at the conveniently measurable rate of 2.2×10^{-4} litres/mole-second in terms of total bromine.

This larger formation constant of the TBABr-bromine complex is also compatible with previously reported work (64, 73) which indicated that the stability of the trihalide ion increased with increasing size and symmetry of the associated cation for solid salts. This work indicates that in solvents of low polarity, even though the salt is ionic, the cation and anion must be very closely associated for the cation to have such a pronounced effect on the stability of the anion. To the author's knowledge it has not been previously noted that a larger and/or

more symmetrical cation increases the stability of the trihalide ion in solution.

For the sake of clarity and convenience to the reader, some of the following material is a review of a portion of the material presented earlier in Section D of the Historical Review. Formation constants of the tribromide ion have been reported previously in non-aqueous solvents (50) by Nelson and Iwamoto. The complex between tetraethylammonium bromide and bromine is reported to have formation constants of $10^{7.3}$, $10^{9.3}$ and 10^7 in nitromethane, acetone and acetonitrile respectively as determined by a voltammetric method. Further, they found that the order of stability of the trihalides is $\text{Cl}_3^- > \text{Br}_3^- > \text{I}_3^-$. This is opposite to the order found in water and opposite to the order observed in the solid salts (64, 73). They state that the expected order is as they have observed. Their rationale for this is as follows. "Because the acid strength, in the Lewis sense, of the three halogens is chlorine $>$ bromine $>$ iodine and the basic strength of the three halides is chloride $>$ bromide $>$ iodide". They account for the order observed in water being the reverse on the basis that water "is a stronger acid than chlorine and a stronger base than chloride ion: therefore, the hydration of both X^- and X_2 increases from the triiodide system to the trichloride system and the stability of the trihalides, accordingly, decreases in the order triiodide $>$ tribromide $>$ trichloride."

They ignore the fact that the stability of the solid salts is opposite to what they predict.

This author disagrees with their statement about the electrophilicity of the halogens. The electrophilicity of the halogen molecule in this reaction is primarily a function of its ability to expand its octet to accommodate the requisite number of electrons. With the halogens, as with all of the other families, the heavier elements show greater tendency to expand their octets than do the lighter. This predicts that the Lewis acid strength is exactly the opposite of what Nelson and Iwamoto claim.

Further, there is strong evidence that the trihalide ions exhibit the same order of stability in the aprotic solvent chloroform as they do in water. Pincock (58) has evaluated spectrophotometrically the formation constant for the trichloride ion in the system $TBACl$ -chlorine in chloroform. A value of 17 litres/mole was obtained, in comparison to 9×10^4 litres/mole for the tribromide ion as determined under similar conditions in this study. This tremendous difference in formation constants is perfectly compatible with halogenation rate studies in chloroform. As has already been mentioned, $TBABr$ has a very large retarding effect on the rate of bromination due to the formation of tribromide ion. If the formation constant for the trichloride ion were larger than for the tribromide ion, $TBACl$ should have an even greater retarding effect on chlorination

than TBABr has on bromination. On the contrary, Pincock (58) has observed that TBACl increases the rate of chlorination in chloroform. Presumably, this increase in the rate of chlorination caused by TBACl is because of an increase in polarity of the solvent with very little of the chlorine complexed.

4. Bromination in Chloroform

The prime objective of the rate studies in chloroform was to determine and account for the effect of pyridinium salts on aromatic bromination in this solvent.

Some of the results in chloroform were presented in Table 8. The results which did not lend themselves to tabulation are described in Section B:5:b of the Method and Results. In summary, it was found that, as in the work in acetic acid, the addition of pyridinium chloride increased the rate of bromination and the addition of pyridinium bromide decreased the rate of bromination when using the same concentration of reactants (ca. 0.2 M in mesitylene and ca. 0.004 M in bromine). This work also points out that there is nothing unique about the ability of a pyridinium salt to increase the rate, as a greater increase in rate was noted for the first part of the reaction when tetrabutylammonium perchlorate (to be referred to as TBAClO₄ from here on) was added. Further it was found that TBABr retards the rate of bromination more effectively than pyridinium bromide (this information and the reason for this effect has already been discussed in the previous section, IV:B:3).

Perhaps, of more interest is the effect of pyridinium bromide on the order of the reaction. It will be recalled that in chloroform the order with respect to bromine is two in the absence of added salts. In addition to decreasing the rate, the presence of pyridinium bromide (0.1 M) was found to change the order with respect to bromine from two to approximately one. 0.1 M pyridinium chloride did not have a large effect on the order. However, the addition of 0.55 M pyridinium chloride resulted in a large contribution from a first-order reaction. It is interesting to note the effect of the different concentrations of pyridinium chloride on the time for 50% reaction. Using approximately the same concentrations of reactants, it was found that the addition of 0.1 M pyridinium chloride decreased the time from ca. 6,000 seconds (in the absence of added salts) to ca. 2,000 seconds. However, the time was only decreased to a slightly lower value (ca. 1,600 seconds) in the presence of a much larger concentration of pyridinium chloride (0.55 M).

To facilitate the discussion of these results the mechanism of bromination will be briefly reviewed once again. The currently accepted mechanism for the un-catalyzed reaction, and for the reaction catalyzed by weak electrophiles such as iodine, involves a rate-determining heterolysis of the bromine-bromine bond in the ArHBr_2 complex. This is followed by a fast step, involving proton loss, to yield the final product.

It has been shown that the rate of the heterolysis step can be greatly increased by an increase in the polarity of the medium, caused by addition of water or salts to the solvent. It has been demonstrated that strong electrophiles such as ferric chloride are capable of altering the mechanism of the un-catalyzed reaction by making the halogen sufficiently electrophilic that heterolysis of the bromine-bromine bond is no longer kinetically important and that the over-all rate is much faster. A kinetic hydrogen-isotope effect could not be found under these conditions. It follows from this brief summary that a compound can increase the rate of reaction (a) by assisting in the heterolysis of the bromine-bromine bond of the ArHBr_2 complex by direct participation in this step, (b) by increasing the electrophilic character of the attacking bromine sufficiently that heterolysis of the bromine-bromine bond is no longer kinetically important or (c) by increasing the polarity of the medium.

Some of the arguments to be presented in the following discussion of these results have been given previously in discussing other work in this thesis, but are included again for the sake of clarity and completeness. The following is a suggested explanation for the results.

It is not likely that a pyridinium salt could act through (b) as this would require a strong electrophile.

Next, consider the possibility of the reaction in the presence of pyridinium chloride being accelerated through (a). Ordinarily, in solvents of low polarity the heterolysis, when it does not take place in an unassisted manner, is considered to be aided by a second bromine molecule acting as an electrophile. Experimental evidence (42) indicates that the pyridinium cation has sufficient electrophilic character, through its pi electron system, to form a weak complex with the iodide ion. As the bromine-bromine bond of the $ArHBr_2$ complex will be polarized in the transition state, the pyridinium cation could form a pi complex with the incipient bromide ion, thereby lowering the energy of the transition state and increasing the rate. Alternatively, the pyridinium cation could increase the rate by forming a hydrogen bond with the incipient bromide ion. However, it does not seem that these two modes can have a significant effect because $TBAClO_4$, which is not capable of hydrogen bonding nor pi complexing with the incipient bromide ion, increased the rate by a much greater amount than pyridinium chloride. Therefore, it seems the increase in rate in the presence of pyridinium chloride must result mainly from an increase in the polarity of the medium. This is supported by the fact that $TBAClO_4$, which increased the rate by a larger amount, must increase the rate by a polarity effect as no other mode of action appears to be available to the latter salt.

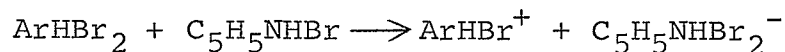
The above discussion could be applied to any pyridinium salt; so, it is now necessary to account for why pyridinium

chloride accelerates and pyridinium bromide retards the rate. Further, it must be explained why TBAClO_4 accelerates more than pyridinium chloride and why TBABr retards more than pyridinium bromide.

It is well known that the tribromide ion is a very much poorer brominating agent than bromine (51). By analogy it is to be expected that Br_2Cl^- will be a poorer brominating agent than bromine. Thus, when a halide salt is present there are two opposing factors to be considered: (a) retardation caused by the formation of a trihalide ion and (b) acceleration caused by an increase in solvent polarity. It is to be expected that pyridinium bromide and pyridinium chloride will have similar effects on the solvent polarity. To account for retardation by pyridinium bromide and acceleration by pyridinium chloride (as noted earlier, this was also observed for the rate studies in acetic acid) it must be postulated that in chloroform the formation constant for complex formation between pyridinium bromide and bromine must be very much greater than that for complex formation between pyridinium chloride and bromine. The formation constant for the latter is not available in any solvent, but the formation constants for the appropriate trihalides in water (using inorganic cations) and the stabilities of the appropriate solid trihalide salts (when comparing salts of the same inorganic cation) support the above postulate. Also in support of this postulate is work done by the author and by

Pincock (already discussed in the previous section, IV:B:3) which gives strong evidence that tribromide ion is very much more stable than trichloride ion in chloroform (the tetrabutylammonium cation was used in both cases). This suggests that tribromide ion is more stable than the dibromochloride ion in chloroform, as in all known cases where tribromide ion is more stable than trichloride ion it has been found that the tribromide ion is also more stable than the dibromochloride ion.

At this point, the mechanism proposed by Yeddanapalli and Gnanapragasam to account for their observed pyridine catalysis in carbon tetrachloride (discussed previously in Section A of the Historical Review) should be commented on. It should be recalled that the author of this thesis was unable to reproduce this work as noted in Section B:6 of the Method and Results. Yeddanapalli and Gnanapragasam attributed the catalytic effect to pyridinium bromide formed from pyridine in the course of the reaction. Pyridinium bromide was considered by them to increase the rate by intervention in the rate-determining step, heterolysis of the bromine-bromine bond of the ArHBr_2 complex.



As can be seen from the above discussion no evidence was obtained in this study for catalysis of this nature.

As mentioned earlier, TBAClO_4 accelerates the rate of bromination in chloroform more than pyridinium chloride does. This can be accounted for on the basis that trihalide formation in the latter case partially offsets the polarity effect. Another factor which may be involved is that the former salt may be more ionic in chloroform and thus have a greater polarity effect.

The fact that TBABr retards bromination more than pyridinium bromide does immediately suggests that the former ties up more bromine than the latter. This has been confirmed experimentally by formation constant determinations (see Section B:5:a of the Method and Results). A value of 198 litres/mole was obtained for the formation constant between pyridinium bromide and bromine, whereas a value of 9×10^4 litres/mole was obtained for that between TBABr and bromine.

As described previously, bromination in the presence of TBAClO_4 was unusual (Figure 13). Bromine was consumed very rapidly at first, and then the later stages of the reaction were extremely slow. This pronounced retardation after about 50% reaction can be accounted for by the very large formation constant for complex formation between TBABr and bromine. It must be argued that HBr (formed in the reaction) reacts with the TBAClO_4 to yield HClO_4 and TBABr . Ordinarily this reaction would not proceed as perchloric acid is a stronger acid than hydrobromic in this medium. However, in the presence of bromine the reaction would be driven to the right because of the strong

tendency for TBABr to complex with bromine. In this manner the bromine is rendered inactive.

As noted above, pyridinium bromide not only retards the rate of bromination, but changes the order of the reaction as well. To understand how this change in order is possible it is necessary to recall that the rate-determining step in bromination is the heterolysis of the bromine-bromine bond of the ArHBr_2 complex. A reaction consisting of an unassisted heterolysis leads to first-order-in-bromine kinetics. A heterolysis assisted by a second molecule of bromine will result in second-order-in-bromine kinetics. If both reactions are involved, mixed first- and second-order kinetics will result. It should be noted that there probably is a very large difference in the character of the first- and the second-order-in-bromine reactions even though the end result in each case is the heterolysis of the bromine-bromine bond. Essentially, the first-order-in-bromine reaction must be an ionization of ArHBr_2 to form ArHBr^+ and Br^- . On the contrary, the second-order-in-bromine reaction must be an electrophilic displacement in which the electrophile ArHBr^+ is displaced by the electrophile Br_2 . It seems reasonable to assume that the former (ionization) will be increased much more than the latter (electrophilic displacement) by an increase in the polarity of the solvent. Both of these reactions involve separation of charge in the transition state, and therefore both will be accelerated by an increase in the polarity of the medium. The products of the

former reaction are the sigma complex ArHBr^+ and Br^- ; the products of the latter are the same sigma complex and Br_3^- . In the former case there will be a much greater charge density in the transition state as Br^- is much smaller than Br_3^- . In order to attain stability through dispersal of charge by solvation, the transition state of the former reaction requires considerably more solvation than the transition state of the latter reaction. Consequently the former reaction will be accelerated more by an increase in polarity than the latter reaction. From this discussion it can be seen that addition of pyridinium bromide will favour the first-order-in-bromine reaction over the second-order-in-bromine reaction.

As pointed out earlier, Josephson, Keefer and Andrews (35) have shown that bromination in pure chloroform is second order in bromine. This is not surprising as it is quite understandable that the unassisted heterolysis could not take place to any great extent, relative to the assisted heterolysis, in a medium of such poor ion-solvating power as chloroform. However, chloroform containing 0.1 M pyridinium bromide has greater ion-stabilizing power and the unassisted heterolysis would be expected to take place more readily. This is supported by the first-order-in-bromine kinetics observed in the presence of 0.1 M pyridinium bromide. Under these conditions the assisted heterolysis will be severely hampered; not only does pyridinium bromide favour the unassisted heterolysis through a polarity effect, but also it retards the assisted heterolysis to

a large extent by complexing most of the bromine (under the conditions employed, only about 5% of the bromine is left un-complexed) so that very little bromine is left to assist in the heterolysis of the bromine-bromine bond of the ArHBr_2 complex.

These arguments can be put on a more quantitative basis. Consider the kinetic expression for mixed first- and second-order-in-bromine kinetics.

$$-dB/dt = k_2MB + k_3MB^2$$

M and B are the concentrations of mesitylene and total bromine respectively in moles/litre, k_2 and k_3 are the second- and third-order rate constants respectively, and t is the time.

Grouping the above expression yields

$$-dB/dt = MB(k_2 + k_3B). \quad (13)$$

From this representation it can be seen that the relative contributions of the two reactions depend on the relative values of k_2 and k_3B . The discussion above requires that k_2 be negligible compared to k_3B when the reaction is carried out in the absence of added salts, but that k_3B be negligible compared to k_2 in the presence of 0.1 M pyridinium bromide. The first problem is to decide what is "negligible" under these circumstances. In the absence of added salts Josephson, Keefer and Andrews (35) and the author both found the bromination to be second order in bromine up to 50% reaction. Beyond that point there was an upward drift in the rate (see Figure 9) which they attributed to a mild catalysis by the hydrogen bromide

produced in the reaction; under these circumstances a small contribution from the first-order-in-bromine term would not be detected. Perhaps 5% would be a reasonable estimate for this contribution, but it might be as high as 10%. In the presence of 0.1 M pyridinium bromide the reaction was first order in bromine to higher conversion (see Figure 10) but the possibility of some contribution from a second-order term (k_3) exists (as was commented on in Section B:5:b of the Method and Results) and this will also be taken as 5%.

Assuming that in the absence of added salts the contribution from the first-order-in-bromine reaction is 5% or less, equation 13 shows that

$$k_2 \leq .05 k_3 B.$$

The initial bromine concentrations in the runs were always around 4×10^{-3} M. For simplification this value will be used for the calculations. The second-order-in-bromine rate constant, k_3 , for the bromination of mesitylene in the absence of salts is 0.18 litres²/mole²-second (see Table 8). It follows that $k_2 \leq 0.36 \times 10^{-4}$ litres/mole-second. Since B will decrease during the run, k_2 would have to be even smaller if the first-order-in-bromine term is not to interfere at later stages in the reaction. Perhaps this accounts, at least in part, for the upward drift in the second-order rate mentioned above.

Pyridinium bromide will have two effects. Like any salt it will increase both k_2 and k_3 (k_2 more than k_3), and by

complexing it will decrease the concentration of free bromine. The former effect can not be predicted quantitatively, since different salts have different effects (see reference 39, where this has been found for different inorganic salts in acetic acid), but the latter can be estimated from the formation constant of 198 litres/mole found for the pyridinium bromide-bromine complex in chloroform (see Section B:5:a of the Method and Results). Use of the above formation constant shows that the addition of 0.1 M pyridinium bromide will reduce the free bromine concentration from 4×10^{-3} to 2×10^{-4} M. When part of the bromine is complexed by pyridinium bromine, it must be realized that the values of $(k_2)_f$ and $(k_3)_f(B_f)$ should be employed if comparisons are to be made with the reaction carried out in the absence of salt. These symbols have the same meaning as in prior usage; (B_f) is the concentration of free bromine, $(k_2)_f$ is the first- and $(k_3)_f$ is the second-order-in-bromine rate constant in terms of free bromine.

Accepting the previously quoted evidence (51) that bromination by the complex is insignificant, and assuming that in the presence of 0.1 M pyridinium bromide the contribution from the second-order-in-bromine reaction is 5% or less, equation 13 shows that

$$(k_3)_f(B_f) \leq .05 (k_2)_f$$

or that $(k_3)_f \leq 250 (k_2)_f$. The observed value of $(k_2)_f$ under these conditions is 45×10^{-4} litres/mole-second (Table 8) so

that $(k_3)_f \leq 1.13$ litres²/mole²-second. Since (B_f) decreases during a run and since small deviations from simple kinetics become detectable in only the later stages of a reaction, $(k_3)_f$ could actually be considerably larger than 1.13 before it would be detectable in the presence of 0.1 M pyridinium bromide.

From these calculations it can therefore be concluded that the change in order of reaction from third to second on adding 0.1 M pyridinium bromide can be accounted for by complex formation, provided that the salt effect produced by this concentration of pyridinium bromide is great enough to increase the second-order rate constant from no more than 0.36×10^{-4} to 45×10^{-4} (i.e. a factor of at least 125) and the third-order rate constant from 0.18 to no less than 1.13 (i.e. a factor of 6 or more). If 10% contributions from the minor reaction (instead of the 5% assumed above) were taken as the detectable limit, these factors would be changed to 63 and 13 respectively. As was pointed out in the arguments above, it is quite reasonable to suppose that k_2 could be increased by much more than k_3 on adding pyridinium bromide to a poor ion-solvating liquid such as chloroform.

An effect, similar to the above, was found by Zimmerman and Berliner (77) in 75% aqueous acetic acid. The order was decreased from mixed first and second with respect to bromine to straight first order on addition of excess sodium bromide. They accounted for their results in a manner similar to the above.

In contrast to the behaviour in the presence of 0.1 M pyridinium bromide, bromination in the presence of 0.55 M pyridinium chloride exhibits a significant contribution from a second-order-in-bromine term (Figure 12). In view of the above discussion regarding change in the kinetic order with added pyridinium bromide, this is exactly what is expected. A quantitative discussion of the results is not possible as the formation constant for complex formation between pyridinium chloride and bromine in chloroform is not available. However, as has already been discussed earlier in this section it appears that this formation constant is much smaller than that between pyridinium bromide and bromine. On this basis the above result can easily be explained. The addition of this large amount of pyridinium chloride increases the rate of the first-order-in-bromine reaction sufficiently that it is now in evidence. However, it appears that the formation constant is sufficiently small that not enough bromine is complexed by pyridinium chloride to reduce the second-order-in-bromine reaction as much as in the pyridinium bromide case even when ca. 5 times more pyridinium chloride than pyridinium bromide is used. It is probable that pyridinium chloride and pyridinium bromide have different salt effects. If this is so, this factor could also contribute to the difference in results.

When the pyridinium chloride concentration is reduced from 0.55 to 0.1 M, the first-order-in-bromine term is not as apparent. A plot of the data (Figure 11) according to a

second-order-in-bromine rate law indicates the reaction is predominantly of this order. The observed deviation after 70% reaction could be caused, at least in part, by the contribution of a first-order-in-bromine reaction. It is readily understandable that there would be a smaller contribution from the first-order term in this case as the lower salt concentration would not aid the first-order reaction as much, and also the second-order-in-bromine reaction would not be hindered as much as there would be less bromine complexed. It should be noted that 0.1 M pyridinium chloride in acetic acid also left the reaction predominantly of the second order in bromine.

As stated at the beginning of this section, the prime objective of the rate studies in chloroform was to determine and account for the effect of pyridinium salts on aromatic bromination in chloroform. In summary, pyridinium bromide was found to retard and pyridinium chloride was found to accelerate bromination. All of the results could be accounted for on the basis of salt effects and complex formation with bromine. No evidence was found for any unique catalytic effect possessed by pyridinium salts.

V. EXPERIMENTAL DETAILS

A. COMMERCIAL CHEMICALS USED

Pyridine

Matheson, Coleman and Bell pyridine (suitable for Karl Fischer Reagent) was used without further purification.

Bromine

'Baker Analyzed' Reagent bromine was used without further purification.

Hydrogen Chloride

Anhydrous hydrogen chloride gas was used directly from a cylinder (Matheson).

Tetrabutylammonium Bromide

Eastman white label tetrabutylammonium bromide (10 g) was recrystallized from a mixture of chloroform (50 ml) and anhydrous ether (200 ml). The salt, on being permitted to cool slowly, crystallized out beautifully. After initial drying the salt was ground finely and dried in an evacuated desiccator. This material melted at 100-101°C. The corresponding literature values are 116-117°C and 101-102°C for a metastable form (1), 118-119°C (12) and 118°C (59).

Tetrabutylammonium Perchlorate

Southwestern Analytical Chemicals (polarographic grade) tetrabutylammonium perchlorate was dried in a vacuum desiccator and used without further purification. The melting point was 212-213°C. Literature values are 207-209°C (21) and 213.3°C (33).

Mesitylene

Matheson, Coleman and Bell mesitylene was purified by distillation through a Wheeler 'All-Glass' GE-125-2H fractionating column rated at better than 90 theoretical plates as determined by a n-heptane-methylcyclohexane mixture, alpha equal to 1.07. The fraction distilling at 164.0-164.2°C was collected.

tert-Butylbenzene

Matheson, Coleman and Bell tert-butylbenzene was used without further purification.

B. COMPOUNDS PREPARED

Pyridinium Bromide

Pyridinium bromide was made essentially by the method of Trowbridge and Diehl (70). Aqueous hydrobromic acid (47%) was added to pyridine until a pH of 5 was reached. This solution was evaporated down until a white slurry was obtained. This was cooled, and the solid filtered out. The solid was sucked dry, washed with ether and placed in a vacuum desiccator. The

melting point was 213-215°C. Corresponding literature values are 200°C (70) and 213-214°C (16).

Pyridinium Chloride

Pyridinium chloride was prepared by passing anhydrous hydrogen chloride through a solution of pyridine (75 g) in anhydrous ether (100 ml). The precipitated pyridinium chloride was filtered and washed with cold ether. The salt was recrystallized twice from 2-propanol and then dried in a vacuum desiccator containing P₂O₅. The melting point was 141-144°C. Literature values are 144.5°C (27) and 140-142°C (16). Found: Cl, 30.56% (potentiometric silver nitrate titration). Calc. for C₅H₆NCl: Cl, 30.66%.

When making up solutions, it was found necessary to weigh this salt in a dry box as it is very hygroscopic.

N-Ethylpiperidinium Chloride

Eastman white label N-ethylpiperidine was distilled and the fraction distilling at 129.0-130.2°C was collected. Anhydrous hydrogen chloride was passed through a solution of this amine (20 ml) in anhydrous ether (50 ml). After cooling in an ice bath, the precipitated N-ethylpiperidinium chloride was filtered, washed with ether and then recrystallized from a 3 : 1 mixture of ligroin (b.p. 60-80°C) and 2-propanol. The salt was dried over phosphorus pentoxide in a vacuum desiccator. The melting point was 231-233°C. Literature value: 224-225°C (41).

Tetrabutylammonium Chloride

The salt was prepared essentially by the method of Umni, Elias and Schiff (71). Silver chloride was prepared by mixing equimolar quantities of sodium chloride and silver nitrate in the dark. The precipitated silver chloride was filtered under vacuum, washed with water and washed once with absolute methanol. A 10% excess of the silver chloride was added to 200 ml of a 1.1 M solution of tetrabutylammonium iodide (Eastman) in methanol. The mixture was left to stand for two days in the dark and then the precipitated silver iodide was filtered. The methanol was evaporated from the filtrate and the tetrabutylammonium chloride crystallized as a glassy solid. It was recrystallized three times from acetone, dried in an Abderhalden drying pistol (acetone was used as the refluxing liquid) containing phosphorus pentoxide and finally transferred to a vacuum desiccator containing the same drying agent. The melting point was 74-75°C. Literature values include 52-54°C (46), 75°C (71), 74.0-74.5°C (12) and 92.5-94.2°C (4). Found: Cl, 12.62% (potentiometric silver nitrate titration). Calc. for $C_{16}H_{36}NCl$: Cl, 12.76%.

It was found necessary to weigh this salt out in a dry box because of its hygroscopic nature.

Compound III

This compound was made essentially by the method of Englert and McElvain (23). These investigators were unable to assign a satisfactory formula.

Bromine (10 g) in acetic acid (10 ml) was added slowly with stirring to a solution of pyridinium bromide (20 g) in acetic acid (30 ml) at 60-65°C. An orange solid began precipitating almost immediately. After allowing the mixture to stand for an hour, the orange solid was filtered out and placed in a vacuum desiccator. The melting point was found to vary with the rate of heating. Typical values are 94-103°C and 100-105°C (the literature value is 101-103°C). A reducible bromine content of 40.1% was found which checks well with the value of 39.7% found by Englert and McElvain.

C. STUDIES IN CONCENTRATED BROMINE SOLUTIONS

Cohen's Method of Bromination

The experimental concentrations Cohen employed for the bromination of benzene, as found in his laboratory manual (14), were 50 g (0.64 moles) of benzene, 120 g (0.75 moles) of bromine and 0.5 g (0.0063 moles) of pyridine. The initial part of the reaction called for a temperature of 25°C. These are the conditions used in the preliminary experiments reported in Section A:1 of the Method and Results and are the experimental conditions meant when the term "Cohen conditions" is referred to.

It is in such a reaction mixture that the dark red solid, I, referred to in Section A of the Method and Results was first noted. As described there, I decomposes to yield II.

Bromination of tert-Butylbenzene in the Presence of Pyridine and Various Salts

A previous bromination of tert-butylbenzene in the presence of pyridine gave a 94% yield of the pure para isomer (19). In this study the reactions were carried out in a 3-necked flask equipped with an efficient condenser and calcium chloride tube. The flask was thermostatted at $35 \pm 0.1^\circ\text{C}$. The reaction was started by mixing 10 ml (0.065 moles) of tert-butylbenzene with 3 ml (0.056 moles) of bromine. Within a series of runs the reaction was carried out with no added substance and with 0.0012-0.0013 moles of pyridine, pyridinium bromide, pyridinium chloride (weighed in a dry box) and tetrabutylammonium bromide. The rates were followed by rapidly withdrawing aliquots with a dropper through a $7/12$ neck of the flask. The aliquots were run into a tared 10 ml volumetric flask, with ground glass stopper, containing about 8 ml of an aqueous ethanolic solution of potassium iodide. The flask was immediately re-weighed and the contents titrated with sodium thiosulfate solution.

Analysis of I

Benzene (15 ml, 0.17 moles), 10 ml (0.19 moles) of bromine and 0.5 ml (0.006 moles) of pyridine were mixed in a 125 ml erlenmeyer flask. After a few minutes the flask was cooled to precipitate the dark red solid. This solid was filtered out

on a sintered glass crucible and a sample (0.35-0.45 g) was quickly transferred to a tared weighing bottle. The weighing bottle was weighed immediately and opened while immersed in 120 ml of an ethanol-water (1 : 1) solution containing 3 g of potassium iodide. This solution was titrated with a standardized sodium thiosulfate solution. This entire procedure was repeated for each sample analyzed.

Determination of the Neutralization Equivalent of II

To the best of the author's knowledge the following method for the determination of the neutralization equivalent in the presence of reducible bromine is original. A direct titration of the acid with base is impossible due to hydrolysis of the bromine. This problem can be circumvented by converting the bromine to bromide by addition of potassium iodide. This method does not change the acid concentration. Iodine does not interfere in the analysis as it does not hydrolyze significantly under the analysis conditions. Because of the iodine color the end-point cannot be determined with an indicator, but the titration is easily followed with a pH meter.

Samples (0.7-0.8 g) were weighed into a dry beaker. Solution was effected by addition of 20 ml of dimethylformamide. A solution of 2 g of potassium iodide in 75 ml of water was added as soon as the sample was dissolved, followed by titration with N/10 KOH.

Determination of Reducible Bromine in II

Samples (0.3-0.5 g) were weighed into a dry beaker (moisture causes loss of bromine). The samples were dissolved in an aqueous ethanolic solution of potassium iodide. The solutions were titrated with N/10 sodium thiosulfate.

Determination of Total Bromine in II

Samples (0.3-0.5 g) were weighed into a dry beaker. The samples were dissolved in 10 ml of a saturated solution of sulfur dioxide in water. A further 50 ml of water was added. The solutions were titrated potentiometrically with N/10 silver nitrate solution using a silver electrode-calomel electrode system.

Preparation of a Complex between Bromine and Pyridinium Chloride

A solution of 10 ml of pyridine in 100 ml of carbon tetrachloride and a solution of 5.1 ml of bromine in 100 ml of carbon tetrachloride were mixed slowly with cooling. The $C_5H_5NBr_2$ (74) which precipitated was filtered out on a sintered glass crucible and washed thoroughly with cold carbon tetrachloride. The product was immediately dissolved in 130 ml of ethylene chloride. Dry hydrogen chloride was passed slowly through. After 5 minutes product began to appear, and after another 3 minutes the reaction was stopped. The product was filtered out and placed in a vacuum desiccator. The orange

solid melted at 87-91°C. The reducible bromine was analyzed for in the same manner as II above. The value obtained was 55.1% whereas $C_5H_5NHClBr_2$ requires 58.0%.

D. PURIFICATION OF SOLVENTS

Acetic Acid

CIL acetic acid was purified by a method similar to that of Orton and Bradfield (54). The acetic acid was refluxed approximately 3 hours with chromic anhydride (2 g/100 ml of acetic acid) and then distilled off. The freezing point of this material was then taken with a Beckman thermometer (calibrated against a platinum resistance thermometer). The water content of the acetic acid was calculated from a knowledge of the freezing point of pure acetic acid, 16.63°C (72), and the fact that the freezing point is lowered 0.2°C for each 0.1% of water (55). Eighty-five per cent of the amount of acetic anhydride required to react with the water was added. This mixture was then refluxed for one hour, followed by distillation through a four foot column of $3/4$ inch diameter packed with glass helices. The fraction distilling at 116.9-117.2°C was collected. Freezing point: 16.55°C.

Chloroform

Fisher U.S.P. Chloroform (0.75% ethanol as preservative) was purified initially by the method of Feiser (25). The chloroform was washed twice with concentrated sulfuric acid,

washed several times with water, dried over calcium chloride and distilled in the dark. The fraction distilling between 60.5-60.7°C was collected. Unfortunately, once the stabilizing ethanol is removed the chloroform is very unstable. It may be suitable for use for 2 or 3 days, but it was found that for the purposes of the work presented in this thesis it could not be depended on for more than a few hours.

It is believed (9, 26, 72) that chloroform reacts slowly with oxygen, or oxidizing agents, when exposed to air and light. The principal products of this decomposition are phosgene, chlorine and hydrogen chloride. Ethanol retards this decomposition, but for the purposes of this work it was necessary to remove it.

It was, therefore, necessary to find a means of storing the chloroform after the ethanol was removed. After some experimentation it was found that purified chloroform remained free from decomposition products for at least two weeks when stored over alumina. (Chloroform containing decomposition products is known to give a positive test (35) to potassium iodide.) It was discovered that two of the steps of Feiser's method of purification may be omitted when the chloroform is to be stored over alumina: washing with water and drying over calcium chloride. The alumina was stirred up and then filtered out just before the chloroform was to be used.

Carbon Tetrachloride

Carbon tetrachloride (1800 ml) was refluxed for 2½ hours with 400 ml of a 5% aqueous sodium hydroxide solution, while being stirred mechanically. The carbon tetrachloride was then washed thoroughly with water and extracted three times with concentrated sulfuric acid. Following this the organic liquid was washed with water and dried over drierite. The carbon tetrachloride was distilled through an insulated 120 cm Vigreux column; the material distilling at 75.5–75.8°C was collected.

Ethylene Chloride

Several variations were tried in the purification of ethylene chloride (Matheson, Coleman and Bell). None of these purifications gave satisfactory material and it was concluded that ethylene chloride was not a satisfactory solvent for the purpose of this work. No experimental results were obtained in this solvent. This is discussed more fully in Section B:4 of the Method and Results. In all cases the ethylene chloride was extracted with concentrated sulfuric acid, washed with water and distilled. Separately tried variations to this procedure included standing with bromine for several hours, distilling from barium oxide, storage over calcium hydride and storage over barium oxide.

E. REACTION RATE MEASUREMENTS IN DILUTE BROMINE SOLUTIONS

Titrimetric

All of the rates followed titrimetrically were of a preliminary nature and were not used for determining rate constants. In such rate studies in benzene and acetic acid the reaction was stopped by delivering aliquots into a solution containing a known excess of arsenious oxide solution. The excess arsenious oxide was then titrated with a potassium bromate solution using methyl orange as an indicator. The rate studies in water solution were followed iodometrically using a sodium thiosulfate solution. In all of these cases the reaction flasks were kept in subdued light.

Spectrophotometric

All reaction rates in chloroform and the reaction rates reported in Table 5 for acetic acid were followed spectrophotometrically. All of the spectrophotometric work in acetic acid was carried out on a Beckman Model DK-1 Spectrophotometer. The instrument was equipped with a Beckman 92527 Temperature Regulated Cell Holder. This attachment was not operated in the intended manner. The control device of this was not used at all, but instead water was pumped through from a constant temperature bath. It was found necessary to circulate cooling water through the lamp housing to avoid an upward drift in temperature. In this way the temperature could be controlled

to $25.0 \pm 0.2^{\circ}\text{C}$. Some of the work in chloroform was carried out on the above Beckman DK-1, and the rest was done on a Beckman DU. This instrument was thermostatted at $25.0 \pm 0.2^{\circ}\text{C}$ by circulating water through its dual thermospacers. Cooling water was passed through the lamp housing. The same rate runs followed on both instruments checked with each other, well within experimental error.

The rates of the uncatalyzed reactions in acetic acid could have been followed titrimetrically, but the reactions with added salts were too fast to follow titrimetrically if the same substrate at the same concentration was to be used. It is known that the rate constants of brominations are affected slightly by the concentration of aromatic substrate (39). It was therefore considered expedient to follow all the rates reported in Table 5 spectrophotometrically.

The spectrophotometric method was chosen over the titrimetric method for the work in chloroform because of the known difficulty (66) of obtaining accurate titration values when following rates in media which are not miscible with water. Apparently the difficulty is because of the heterogeneous quenching mixture. While the halogen is being destroyed by the aqueous quenching solution, it is believed that traces of water introduced into the non polar layer accelerate the rate of halogenation.

In both acetic acid and chloroform practically all of the rate runs were done in duplicate. The reactions were carried out in a darkened room to prevent light-catalyzed halogenations and, in the case of the runs in chloroform, to help prevent photodecomposition of the solvent.

As indicated by constant absorbance values, both solvents were found to be stable to bromine within experimental error, under the experimental conditions employed, for the time of the slowest rate runs (ca. 6 hours). Using the same technique, the salts employed as catalysts were found to be stable to bromine since solutions containing bromine and these salts were optically stable under the conditions of the rate runs.

A rapid method of starting the reactions was necessary in order to be able to get initial points for the very fast reactions. Also, for this reason, only the DK-1 was used for very fast reactions as this instrument is capable of obtaining earlier readings, because of its recording system, than are possible with the DU. A 1 ml aliquot of the combined salt and mesitylene solution was pipetted into a cuvette already in the instrument. When this solution came to equilibrium temperature (after ca. 15 minutes), 2 ml of a previously thermostatted bromine solution were pipetted into a cuvette to start the reaction. In some cases 1 ml of the halogen solution and 2 ml of the other solution were used, but in all cases the halogen was pipetted in last to start the reaction. After the second

aliquot was added to the cuvette, the cuvette was rapidly removed, shaken and returned to the spectrophotometer.

The reactions in acetic acid were followed at around 400 millimicrons and those in chloroform at around 440 millimicrons. The initial halogen concentration was obtained by titration of an aliquot from the stock solution. The absorptivity was determined from this initial halogen concentration and the initial absorbance (obtained by extrapolating the rate data back to zero time).

F. EQUILIBRIUM CONSTANT MEASUREMENTS

Measurements were made in order to determine the equilibrium constants between pyridinium bromide and bromine and between tetrabutylammonium bromide and bromine, both in chloroform.

Preliminary data for the equilibrium constant determinations were obtained using a Beckman DK-1 Spectrophotometer. Solutions of various concentrations were scanned in order to determine suitable concentrations and wavelengths. Also of prime consideration was the choice of conditions which would give the most optically stable solutions. Stability measurements were carried out on a Beckman DU (thermostatted at $25.0 \pm 0.2^\circ\text{C}$), as were the actual measurements used in calculating the equilibrium constants.

Because of the instability of some solutions it was necessary to obtain the absorbance readings as rapidly as possible. Fresh stock solutions were made up immediately before the preparation of each final solution used in obtaining an absorbance value. The absorbance reading was taken immediately after preparation of the solution.

Solutions of the salts were made by weighing out the salts in volumetric flasks and diluting to the mark. The bromine stock solutions were made by adding neat bromine to chloroform. The concentration of bromine was evaluated by determining the absorbance of the solution and making use of the absorptivity which had been determined very accurately. The final solutions were made by mixing and dilution of appropriate amounts of the stock solutions.

The exact experimental conditions (concentrations and wavelengths used) and the absorbance values obtained are given in Tables 6 and 7.

VI. SUMMARY

A. WORK IN CONCENTRATED BROMINE SOLUTIONS

1. Two solid pyridine-bromine complexes were isolated in the work in concentrated bromine solutions. The first was very unstable; a molecular composition corresponding to $C_5H_5NHBr(Br_2)_2$ has been postulated. The first compound decomposed to the second on standing or being washed with carbon tetrachloride. The second was quite stable; strong evidence has been presented for a stoichiometry corresponding to $(C_5H_5NHBr_3)_2C_5H_5NHBr$.

2. It was observed that in the usual solutions employed for pyridine-catalyzed halogenations in concentrated bromine solutions a two phase system was present; either a solid and a liquid or two liquids were present depending on the temperature. It is argued that catalysis in the former of these systems is a surface effect and that catalysis in the latter is a medium effect in which bromination takes place faster in the more polar second layer. Experimental work with this system and with added amine salts supports this viewpoint.

B. WORK IN DILUTE BROMINE SOLUTIONS

1. Addition of pyridine to both benzene and water solutions decreased the rate of aromatic bromination, indicating that $C_5H_5NBr_2$ is a poorer brominating agent than bromine, if it brominates at all.

2. Addition of pyridine to acetic acid increased the rate of aromatic bromination. This was interpreted as being the result of pyridine increasing the polarity of the solvent and thereby the rate.

3. Bromination of mesitylene in acetic acid has been shown to be accelerated by added salts, such as pyridinium chloride, tetrabutylammonium chloride and N-ethylpiperidinium chloride. This indicates there is nothing unique about the ability of a pyridinium salt to increase the rate. The results could be accounted for on the basis of a salt effect.

4. Bromide salts used (pyridinium bromide in acetic acid; pyridinium bromide and TBABr in chloroform) were found to decrease the rate of bromination. This is believed to be caused by complexing of bromine by bromide ion to form tribromide ion which is a much poorer brominating agent than bromine.

5. The formation constants have been determined for complex formation between pyridinium bromide and bromine (198 litres/mole) and between TBABr and bromine (9×10^4 litres/mole) in chloroform. This large difference in formation constants is perfectly compatible with the different degrees to which these two salts retard bromination in chloroform. The argument that the complex is that of the tribromide ion in both cases is presented.

6. Contrary to the work of Nelson and Iwamoto (50), strong evidence has been presented that the trihalide ions

exhibit the same order of stability in the aprotic solvent chloroform as they do in water, i.e. $I_3^- > Br_3^- > Cl_3^-$. This evidence is based on both formation constant determinations and the relative retarding effect of TBACl on chlorination and TBABr on bromination.

7. Bromination of mesitylene in chloroform has been shown to be accelerated in the presence of pyridinium chloride and in the presence of $TBAClO_4$. This is believed to be a salt effect rather than a specific intervention of the salt in the transition state of the rate-determining step.

8. As well as retarding the rate of bromination of mesitylene in chloroform, the presence of pyridinium bromide (0.1 M) has been found to change the order with respect to bromine from two to approximately one. This can be accounted for quantitatively by taking into account the formation constant for complex formation between pyridinium bromide and bromine and by postulating reasonable rate increases (because of the increase in polarity of the medium) for each of the first- and second-order reactions.

REFERENCES

1. Accascina, F., Petrucci, S., and Fuoss, R. M. J. Am. Chem. Soc. 81, 1301 (1959).
2. Acheson, R. M. An Introduction to the Chemistry of Heterocyclic Compounds. Interscience Publishers Inc., New York. 1960. p. 166.
3. Acheson, R. M., Hoult, T. G., and Barnard, K. A. J. Chem. Soc. 4142 (1954).
4. Allerhand, A., and von Ragué Schleyer, P. J. Am. Chem. Soc. 85, 1233 (1963).
5. Andrews, L. J., and Keefer, R. M. Molecular Complexes in Organic Chemistry. Holden-Day, Inc., San Francisco, U.S.A. 1964. p. 2.
6. Benesi, H. A., and Hildebrand, J. H. J. Am. Chem. Soc. 71, 2703 (1949).
7. Berliner, E. Progress in Physical Organic Chemistry. Interscience Publishers, New York. 2, 253 (1964).
8. Berliner, E., and Beckett, M. C. J. Am. Chem. Soc. 79, 1425 (1957).
9. Bogendorf, K. Deutsche Apotheker-Zeitung, 44, 351 (1929).
10. Briegleb, G. Elektronen-Donator-Acceptor-Komplexe. Springer-Verlag, Berlin. 1961. p. 195.
11. Brown, H. C., and Stock, L. M. J. Am. Chem. Soc. 79, 1421 (1957).
12. Buckson, R. L., and Smith, S. G. J. Phys. Chem. 68, 1875 (1964).
13. Carter, S., Murrell, J. N., and Rosch, E. J. J. Chem. Soc. 2048 (1965).
14. Cohen, J. B. Practical Organic Chemistry, Third Edition. Macmillan and Co., London. 1924. p. 155.
15. Conrow, K., Johnson, G. D., and Bowen, R. E. J. Am. Chem. Soc. 86, 1025 (1964).
16. Cook, D. Can. J. Chem. 39, 2009 (1961).

17. Cross, W. E., and Cohen, J. B. Proc. Chem. Soc. 15 (1908).
18. Daniele, G. Gazz. Chim. Ital. 90, 1585 (1960).
19. de la Mare, P. B. D., and Harvey, J. T. J. Chem. Soc. 131 (1957).
20. de la Mare, P. B. D., and Ridd, J. H. Aromatic Substitution. Butterworths Scientific Publications, London. 1959.
a) p. 109, b) p. 118, c) p. 120 and d) p. 123.
21. Deno, N. C., and Berkheimer, H. E. J. Org. Chem. 28, 2143 (1963).
22. Eisch, J. J., and Jaselskis, B. J. Org. Chem. 28, 2865 (1963).
23. Englert, S. M. E., and McElvain, S. M. J. Am. Chem. Soc. 51, 863 (1929).
24. Ferguson, N. L. The Modern Structural Theory of Organic Chemistry. Prentice-Hall, Inc., Englewood Cliffs, N.J., U.S.A. 1963. Section 1.5.2, p. 103.
25. Fieser, L. F. Experiments in Organic Chemistry, Third Edition, Revised. D. C. Heath and Company, Boston. 1957.
26. Gillo, L. Ann. Chim. 12, 281 (1939).
27. Goffman, M., and Harrington, G. W. J. Phys. Chem. 67, 1877 (1963).
28. Gould, E. S. Mechanism and Structure in Organic Chemistry. Henry Holt and Company, New York. 1959. p. 442.
29. Grovenstein, E., and Aprahamain, N. S. J. Am. Chem. Soc. 84, 212 (1962).
30. Hammond, P. R. J. Chem. Soc. 479 (1964).
31. Hickinbottom, W. J. Reactions of Organic Compounds. Longmans, Green and Co., London. 1936. p. 43.
32. Hine, J. Physical Organic Chemistry, Second Edition. McGraw-Hill Book Company, Inc., New York. 1962. p. 359.
33. Inami, H. V., Bodenseh, H. K., and Ramsey, J. B. J. Am. Chem. Soc. 83, 4745 (1961).
34. Johnson, G. D., and Bowen, R. E. J. Am. Chem. Soc. 87, 1655 (1965).

35. Josephson, R., Keefer, R. M., and Andrews, L. J.
J. Am. Chem. Soc. 83, 2128 (1961).
36. Josephson, R., Keefer, R. M., and Andrews, L. J.
J. Am. Chem. Soc. 83, 3562 (1961).
37. Keefer, R. M., and Andrews, L. J. J. Am. Chem. Soc.
72, 4677 (1950).
38. Keefer, R. M., and Andrews, L. J. J. Am. Chem. Soc.
78, 3637 (1956).
39. Keefer, R. M., Ottenberg, A., and Andrews, L. J. J. Am.
Chem. Soc. 78, 255 (1956).
40. Ketelaar, J. A. A., van de Stolpe, C., Goudsmit, A.,
and Dzcubas, W. Rec. Trav. Chim. 71, 1104 (1952).
41. Kornfield, E. C. J. Org. Chem. 16, 131 (1951).
42. Kosower, E. M., and Burbach, J. C. J. Am. Chem. Soc.
78, 5838 (1956).
43. Krause, E. Ber. 56B, 1801 (1923).
44. Longstaff, J. V. L., and Singer, K. The Analyst, 78,
491 (1953).
45. McElvain, S. M., and Goese, M. A. J. Am. Chem. Soc.
65, 2227 (1943).
46. McMichael, K. O., and Clement, R. A. J. Org. Chem. 26,
620 (1961).
47. Melander, L. Arkiv Kemi, 2, 213 (1950).
48. Merker, P. C., and Vona, J. A. J. Chem. Ed. 26, 613
(1949).
49. Nakagawa, T. W., Andrews, L. J., and Keefer, R. M.
J. Phys. Chem. 61, 1007 (1957).
50. Nelson, I. V., and Iwamoto, R. T. J. Electroanalytical
Chem. 7, 218 (1964).
51. Norman, R. O. C., and Taylor, R. Electrophilic Substitution
in Benzenoid Compounds. Elsevier, Amsterdam. 1965.
p. 130.
52. Olah, G. A. Organic Reaction Mechanisms, The Lectures
Delivered and Synopses of Papers Read at an International
Symposium held at Cork, Ireland, on 20th-25th July, 1964.
Special Publication No. 19. The Chem. Soc. London. p. 21.

53. Olah, G. A., Kuhn, S. J., Flood, S. H., and Hardie, B. A. J. Am. Chem. Soc. 86, 1039 (1964).
54. Orton, K. J. P., and Bradfield, A. E. J. Chem. Soc. 960 (1924).
55. Orton, K. J. P., and Bradfield, A. E. J. Chem. Soc. 983 (1927).
56. Pershina, L. A., and Borodina, I. M. Izv. Tomskogo Politekhn. Inst. 102, 90 (1959). Chem. Abstr. 58, 11250f (1963).
57. Person, W. B. J. Am. Chem. Soc. 87, 167 (1965).
58. Pincock, J. A. M.Sc. Thesis. University of Manitoba. 1966.
59. Reynolds, M. B., and Kraus, C. A. J. Am. Chem. Soc. 70, 1709 (1948).
60. Rose, N. J., and Drago, R. S. J. Am. Chem. Soc. 81, 6138 (1959).
61. Rosenmund, K. W., and Kuhnhenh, W. Ber. 56B, 1262 (1923).
62. Schlafer, H. L. Komplexbildung in Losung. Springer-Verlag, Berlin. 1961.
63. Scott, R. L. Rec. Trav. Chim. 75, 787 (1956).
64. Sidgwick, N. V. The Chemical Elements and their Compounds, Vol. II. The Clarendon Press, Oxford. 1950. p. 1190.
65. Stock, L. M., and Brown, H. C. Advances in Physical Organic Chemistry. Academic Press, New York. 1, 35 (1963).
66. Stock, L. M., and Himoe, A. J. Am. Chem. Soc. 83, 4605 (1961).
67. Taylor, T. W. J., and Baker, W. Sidgwick's Organic Chemistry of Nitrogen. The Clarendon Press, Oxford. 1937. p. 522.
68. Tronov, B. V., and Loginova, V. F. Dokl. 2-oi (Vtorio) Mezhvuz Konf. po Khim. Organ. Kompleksn Soedin. (Tomskii Univ., Tomsk), 69 (1963). Referativnyi Zhurnal, Khimiia, 22B440 (1964). Chem. Abstr. 62, 11708e (1965).
69. Trotter, P. J., and Hanna, N. W. J. Am. Chem. Soc. 88. 3724 (1966).

70. Trowbridge, P. F., and Diehl, O. C. J. Am. Chem. Soc. 19, 558 (1897).
71. Umni, A. K. R., Elias, L., and Schiff, H. I. J. Phys. Chem. 67, 1216 (1963).
72. Weissberger, A., Proskauer, E. S., Riddick, J. A., and Toops, E. E. Technique of Organic Chemistry, Vol. VII: Organic Solvents, Second Edition. Interscience Publishers, Inc., New York. 1955.
73. Wiebenga, E. H., Havinga, E. E., and Boswijk, K. H. Adv. Inorg. Chem. Radiochem. 3, 133 (1961).
74. Williams, D. J. Chem. Soc. 2783 (1931).
75. Yagi, Y., and Popov, A. I. J. Am. Chem. Soc. 87, 3577 (1965).
76. Yeddanapalli, L. M., and Gnanapragasam, N. S. J. Ind. Chem. Soc. 36, 745 (1959).
77. Zimmerman, U. P., and Berliner, E. J. Am. Chem. Soc. 84, 3953 (1962).
78. Zollinger, H. Advances in Physical Organic Chemistry. Academic Press, New York. 2, 163 (1964).