AN INVESTIGATION OF THE WOHL ZIEGLER REACTION

PART I

AN INVESTIGATION OF THE CARBONYL ABSORPTION BAND OF A SERIES OF AMIDES AND N-BROMOAMIDES

PART II

DECOMPOSITION OF AND BROMINATION WITH A SERIES OF N-BROMOAMIDES

Thesis for the Degree of Ph. D.
MICHIGAN STATE UNIVERSITY
John F. Regan
1957

MICHIGAN STATE UNIVERSITY
OF AGRICULTURE AND APPLIED SCIENCE
DEPARTMENT OF CHEMISTRY
EAST LANSING, MICHIGAN

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A THESIS

Submitted to the School for Advanced Graduate Studies of Michigan
State University of Agriculture and Applied Science
in partial fulfillment of the requirements
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DOCTOR OF PHILOSOPHY

Department of Chemistry

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AN ABSTRACT

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ABSTRACT

PART I

The infrared spectra of a series of amides and N-bromoamides were studied with particular emphasis on the carbonyl band. This work was carried out to determine if some property revealed by the spectra could be related to the varying behavior of the N-bromoamides as brominating agents. The carbonyl band was chosen since any electrical effects influencing the nature of the nitrogen bromine bond due to variations in the structure of N-bromoamides would be transmitted through the carbonyl group of such compounds.

The following compounds were studied: acetamide, chloroacetamide, dichloroacetamide, trichloroacetamide, ethoxyacetamide, formamide, trifluoroacetamide, propionamide, phenylacetamide, benzamide, N-bromo mono, di and trichloroacetamides. Carbon tetrachloride and chloroform were used as the solvents.

The absolute integrated absorption intensities, peak frequencies and the shape of the absorption curve of the carbonyl band were studied. The apparent absolute intensities were calculated from the area under the absorption band curve and corrected to give the true intensity value.

A linear relationship was obtained between the absolute intensity and peak frequency values for the amides with the exception of trifluoroacetamide, formamide and ethoxyacetamide. In these cases,

other effects besides the electronegativity of the substituent groups are present. This linear relationship was also exhibited by the N-bromoamides studied. The N-bromoamides have approximately the same carbonyl peak frequency but a much smaller intensity than their corresponding parent amides.

The absolute intensity values of the carbonyl band, in the amides and their N-bromoderivatives, were found to be higher and their peak frequencies lower in chloroform than in carbon tetrachloride.

The dissymmetry of the carbonyl absorption curves of some of the amides suggested that for these amides more than one form of the normal vibration for the carbonyl group exists. This was attributed to the presence of the bulky groups on the carbon alpha to the carbonyl group causing a steric inhibition to rotation of this alpha carbon resulting in certain favored rotational positions of the alpha carbon with respect to the plane of resonance of the amide group.

PART II

Toluene was brominated in the dark by N-bromo mono, di and trichloroacetamide and bromine at two temperatures, 40° and 80°C., using equivalent concentrations of all the reactants in each reaction. The N-bromoamides were prepared by adding bromine to a mixture of the amide and silver oxide in trifluoroacetic acid. Attempts to prepare N-bromoacetamide, N-bromoethoxyacetamide and N-bromophenylacetamide by this method was unsuccessful and led to decomposition of the amide.

The extent of side chain and ring bromination was followed by isolating the reaction products and analyzing the mixture. A material balance of at least 99 per cent of the bromine was attained in the reactions at 80°C. which were allowed to go to completion. A material balance of 85 to 99 per cent was attained in the reactions at 40°C. which were allowed to run for twenty-four hours and were incomplete.

The extent of side chain bromination at the two temperatures 40 and 80°C. decreased in the following order, bromine > N-bromomonochloroacetamide > N-bromodichloroacetamide > N-bromotrichloroacetamide.

In the reactions at 40°C., which were incomplete, free bromine was isolated in each case.

Among the N-bromoamides the N-bromotrichloroacetamide showed the fastest rate of reaction and the N-bromomonochloroacetamide the slowest rate of reaction.

The results obtained in the thermal and photochemical decomposition of the N-bromoamides were carried out; were not completely reproducable. However, N-bromomonochloroacetamide showed the fastest rate of decomposition and N-bromotrichloroacetamide the slowest rate. The bromine formed during the decomposition was found to be complexed with some other compound formed during the decomposition. The decomposition reaction was also determined to be autocatalytic in nature.

A mechanism of bromination with N-bromoamides involving the homolytic and heterolytic dissociation of the nitrogen bromine bond as well as the formation of bromine and a bromine complex was proposed

based on the correlation of the infrared, decomposition and bromination data.

N-bromosuccinimide and N, N-dibromodimethylhydantoin were allowed to react with cyclohexene in refluxing chloroform and carbon tetrachloride. In chloroform only 1,2 dibromocyclohexane was isolated. In carbon tetrachloride 3-bromocyclohexene and 1,2 dibromocyclohexane were isolated. The N-bromosuccinimide gave 63 per cent allylic bromination and a smaller amount of tarry residue than N, N-dibromodimethylhydantoin which gave 55 per cent allylic bromination.

Nitrogen sulfide tetrabromide, $N_4S_4Br_4$, was prepared and allowed to react with cyclohexene. A small amount of allylic bromination occurred, but mainly 1,2 dibromocyclohexane was obtained. Phosphonitrilic bromide was prepared and allowed to react with cyclohexene. Allylic bromination or bromine addition did not occur.

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PART I

AN INVESTIGATION OF THE CARBONYL ABSORPTION BAND OF A SERIES OF AMIDES AND N-BROMOAMIDES

INTRODUCTION

INTRODUCTION

The Wohl Ziegler reaction involves the reaction of an N-bromoamide or imide with an unsaturated compound having a methyl or methylene group adjacent to the double bond as in toluene or cyclohexene to introduce a bromine atom in the allylic position. In connection with making a comparison of the brominating properties of several N-bromoamides it seemed advisable to study their structures and the structures of the amides from which they were derived for the purpose of determining how variations in the groups attached to the carbonyl group would effect both the brominating properties and infrared spectra, particularly the carbonyl band, of such compounds.

The N-bromoamides and imides are capable of allylic bromination as well as nuclear bromination. This was established by the work of Buu-Hoi (1) who studied the action of N-bromosuccinimide on a wide variety of benzene and naphthalene derivatives, notably ethers. The dual brominating character of N-bromoimides has more recently been observed in thiophene (2) and its methyl derivatives (3) where both side chain and nuclear bromination have been observed. The reactions of the N-bromoamides and imides and the mechanism of the reaction are discussed at length in the second part of this thesis. As an aid in an attempt to elucidate the mechanism of the Wohl Ziegler reaction the effects of variations in the structure of the brominating agent on the reaction were studied.

This was approached by a study of the infrared absorption of some typical Wohl Ziegler allylic brominating agents and their parent amides with particular reference to the carbonyl group. The parent amides were included in the investigation so that if a correlation existed between the infrared absorption spectra of the N-bromoamides and their brominating properties, and this correlation was exhibited also by the parent amides, it would be possible from the infrared absorption spectra of the amides to predict the brominating properties of other N-bromoamide.

It was expected that any electrical effects influencing the nature of the nitrogen halogen bond due to variations in the structure of either amides or imides would be transmitted through the carbonyl group of such compounds. Thus, the relative tendencies of the nitrogen bromine bond of the N-bromoamides or imides to undergo homolytic or heterolytic dissociation should be indicated in variations of the infrared absorption band of the carbonyl group in such compounds. Further, it was hoped that some correlation could be found between variations in the infrared absorption of the carbonyl group and the brominating activity of the allylic bromination agents. Thus, this part of the thesis deals with a study of the infrared absorption spectra, particularly the carbonyl band, of some amides and their N-bromo derivatives. The absolute integrated absorption intensities, peak frequencies and the shape of the absorption curve of the carbonyl band were studied.

HISTORICAL

HISTORICAL

The intensity of an infrared absorption band is proportional to the square of the oscillating dipole moment for that vibration of the molecule giving rise to the absorption band (4). The dipole moment change (4) is given by the expression, $(\partial u/\partial Q)$, where u is the molecular dipole moment and Q is the normal coordinate describing the particular vibration. The integrated intensity for a band has been shown to be proportional to $(\partial u/\partial Q)$ (25) with respect to the normal coordinate of the vibration. The correlation of the latter quantity with known or calculable molecular properties has not as yet proven very satisfactory. Barrow (4) demonstrated the relationship between the resonance energy and the intensities of the carbonyl group absorption for a variety of compounds with such a group present.

Wulf and Liddel (5,6) discussed the nitrogen-hydrogen, oxygen-hydrogen and carbon-hydrogen bond absorptions for a variety of compounds and the manner in which the position, shape and intensity of these absorptions are dependent on the neighboring groups attached to such bonds. The relationship between the electronegativities of adjacent substituents and the stretching frequency of the carbonyl group of esters, acid halides and aldehydes was shown by Kagarise (7).

There have been numerous other instances reported in the literature dealing with integrated intensity measurements in infrared absorption spectra such as Ramsay's work (8) with the ketosteroids and the investigations of Francis on the carbon-hydrogen bond in aliphatic hydrocarbons (9) and ketones (10).

No systematic investigation of the integrated intensities of the carbonyl group of amides or N-bromoamides appears in the literature. In fact most of the spectroscopic work carried out on the amide group has been with proteins and other biologically important compounds. Considerably less data are available on the spectra of simpler amides. Bushwell, Rodebush and Roy (11) have conducted a thorough spectroscopic study of amide association in the near infrared region. Recently many amides and N-substituted amides have been extensively studied in the 6 micron region by Lenormant (12,13,14). His results have rather definitely established the keto form as being predominant in the solid state. Lenormant (15) has also confirmed the previous assignment of bands in the 3 micron region to the nitrogen-hydrogen fundamental vibrations by substituting deuterium for the hydrogens on the nitrogen atom and observing a consequent shift in these bands to around 4 microns. Richards and Thompson (16) have conducted the most detailed spectroscopic study of the amides thus far and have been able to interpret their data from a consideration of the keto form and its resonance dipolar structure. Senti and Harker (17) have conducted an X-ray analysis of the crystal structure of acetamide and have found it to exist only in the keto form. They also concluded that the molecule was planar with respect to the carbon, nitrogen and oxygen atoms and that the molecules are associated in ring polymers through nitrogen-hydrogen-oxygen bridges.

Recently Park, Lacher and Tompkin (18) investigated the nitrogen hydrogen fundamental band, 2.93 microns, of a series of alpha halogen N-bromoamides and related the molar extinction coefficient to the brominating activity of the nitrogen bromine bond.

DISCUSSION

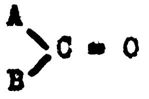
DISCUSSION

For molecules of the type,  $\overset{A}{\underset{B}{}}\!>C=O$, the absorption band associated with the carbonyl stretching is the result of a normal vibration involving a carbon oxygen stretching and some combination of stretching and bending of the C-A and C-B bonds (30). The actual form which the vibration assumes for a particular molecule is dependent on the masses of the atoms or groups A and B, and on the force constants for the bonds C-A and C-B.

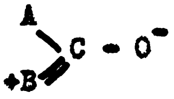
In any interpretation of frequency and intensity changes resulting from structural modifications two factors must be considered. First, the form of the normal vibration and any changes in it occasioned by structural variations, and secondly, electron distribution in the molecule and the way in which it is affected by changing the substituents. These two factors are not independent, since the form of the normal vibration is dependent on the force constants of the bonds which in turn are determined by the electron distribution.

The frequency of a vibration is determined by the masses of the vibrating atomic species and by the force constants for the bands involved in such a vibration. In quinones where the motion can be assumed to be all carbon oxygen stretching, the carbonyl stretching frequency is linearly related to the calculated carbonyl bond order (31). For a series of ring substituted acetophenones, where a mass effect due to ring substitution is negligible, there is a nearly linear relationship between the Hammett ρ values for substituents and the frequency of the carbonyl band (32). From the direction of change it may be inferred that the frequency of the carbonyl stretching vibration in a series of compounds increases with increasing electron density in the carbonyl bond in the ground state of the molecule.

Shifts in carbonyl frequency in terms of the electronic structures involved have more recently been considered (33). For the carbonyl group in amides where the carbonyl group is conjugated with an electron donor group the most important resonating forms are considered to be, in addition to the ionic form inherent in the carbonyl group itself, of the following types:


(a)

and


(b)

Thus, it is to be expected that stretching of the carbonyl bond will lead to an electronic structure of the molecule with a larger contribution from the charge separated canonical form (b) than in the molecule with equilibrium bond lengths. This increase in contribution from the ionic form will depend upon the availability of such a charge separated electronic configuration. This effect would result in amides having lower frequencies than esters and other substances in which there is not such an availability of a charge separated canonical form.

Recently Kogarise (7) demonstrated a linear relationship between the effective electronegativities of adjacent substituents and the

stretching frequency of the carbonyl group. This relationship was demonstrated for aldehydes, acid halides and esters.

In Figure I is shown a plot of the amide carbonyl frequencies versus the effective electronegativities for those amides in Table III whose effective electronegativities were either known or could be calculated from the data of Kagarise (7). Only the values for the R group of the $RCONH_2$ structure were used. The values which were calculated were those for propionamide and ethoxyacetamide in which the R group had more than one carbon atom. The amides included in Figure I are; a, acetamide; b, propionamide; c, ethoxyacetamide; d, monochloroacetamide; e, formamide; f, dichloroacetamide; g, trichloroacetamide; and h, trifluoroacetamide.

The curve strongly suggests that there is a linear relationship between the carbonyl stretching frequency for the amides and the effective electronegativities of the substituent groups. The three exceptions are formamide, ethoxyacetamide, and trifluoroacetamide. Very probably the ethoxyacetamide is low because of the electronegativity value, 1.81, used for the ethoxy group in the calculation of the effective electronegativity of the R group. This value is the one used for esters where both an inductive and mesomeric effect of the ethoxy group are possible. However, in ethoxyacetamide only the inductive effect of the ethoxy group is present and the value of the effective electronegativity should be higher, probably approaching the value for chlorine. In the case of formamide undoubtedly the

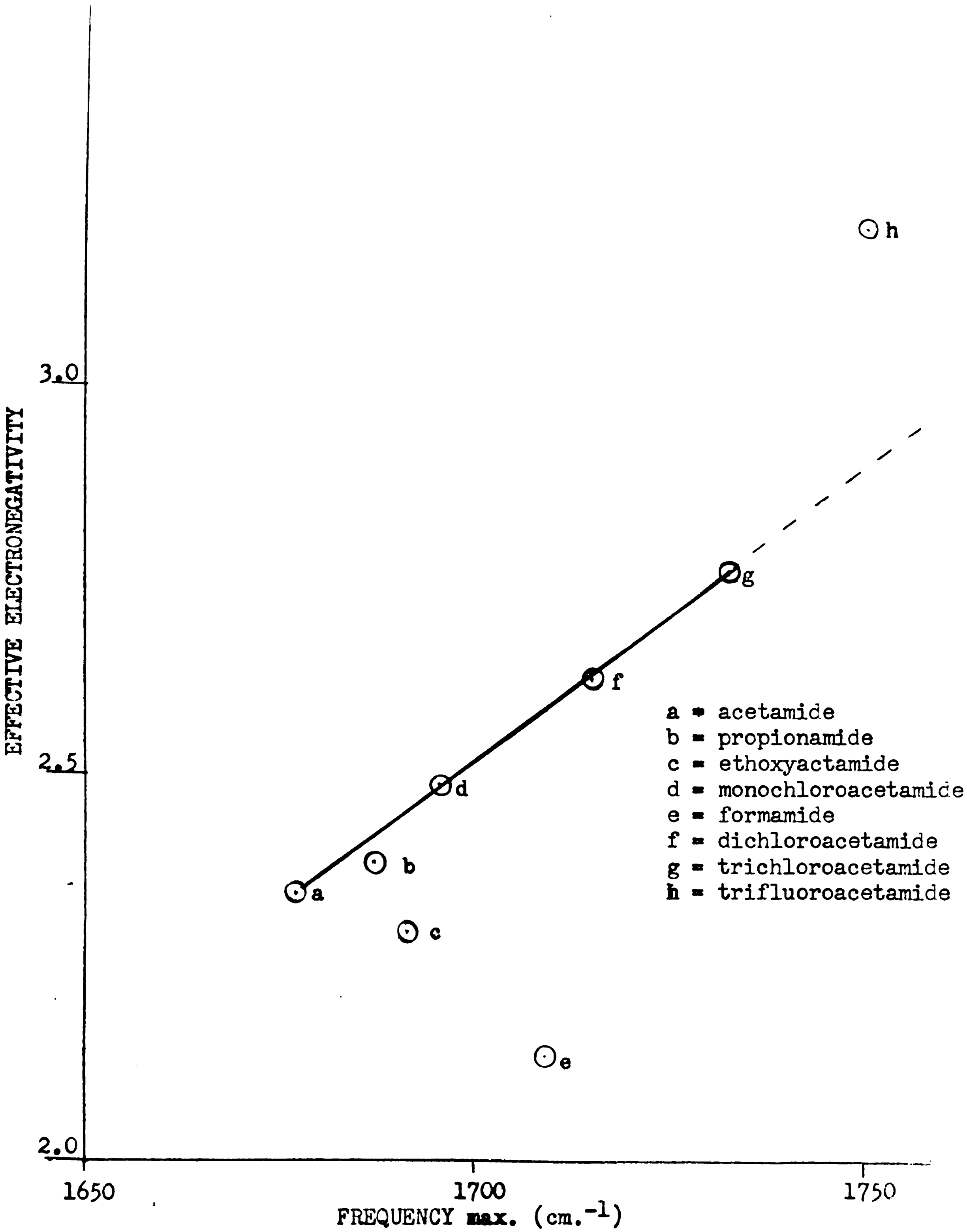


FIGURE I. EFFECTIVE ELECTRONEGATIVITY VERSUS CARBONYL PEAK FREQUENCY FOR A SERIES OF AMIDES frequency is out of order. Inspection of the frequencies shows that the formamide frequency is higher than the frequency for the chloroacetamide. As a result of the inductive effect due to the chlorine atom in chloroacetamide the opposite would be anticipated. This may be due to a mass effect in which it can no longer be assumed that the motion associated with the carbonyl vibration is due solely to carbon oxygen stretching alone. Some possible explanations for the deviations of the trifluoroacetamide will be mentioned in the discussion of intensity values. It is of interest to note that a plot of effective electronegativity versus frequency for the esters which correspond to the above amides with the exception of propionamide and ethoxyacetamide showed a similar linear relationship (7). It can be concluded with a reasonable degree of certainty that the carbonyl stretching frequency is linearly related to the inductive effect of the substituent groups for the above amides.

The integrated intensity of an infrared absorption band is proportional to the square of the oscillating dipole moment for that vibration of the molecule giving rise to the absorption band. This dipole moment change is given by the expression $(\partial u/\partial Q)$, where u is the molecular dipole moment and Q is the normal coordinate describing the particular vibration in question (25). When the relationship between the normal coordinates and the internal coordinates are known, the quantity, $(\partial u/\partial Q)^2$, for a stretching mode and u_r for a bending mode where u is the bond coordinate may be determined.

The correlation of the quantity, $(\partial u/\partial Q)^2$, with known or calculable molecular properties has not as yet proven very satisfactory. The concept that the change in dipole moment with bond stretching might be interpreted on the basis of fixed electronic charges on the nuclei was immediately shown to be insufficient by the large values; that is, greater than an electronic charge, found for $\partial u/\partial r$ where r is a bond length for certain multiple bonded molecules (35). In fact, these measurements suggest that the increased contribution of charge separated resonance forms, like (b) above, would explain the high values of the change in dipole moment with bond stretching. Barrow (4) in recent studies has demonstrated a correlation between resonance energies and the intensities of the carbonyl absorption band by assuming that the resonance energy due to carbonyl conjugation is a measure of the availability of such a canonical form as (b). Ramsay (8) observed that conjugation in the keto steroids increased the intensity of absorption.

Figure II is a plot of the absolute intensity values versus the frequency for the amides listed in the Tables III and IV. The method of determining the absolute intensity is outlined in the experimental section of Part I of this thesis. The compounds used in determining this curve are; a, benzamide; b, acetamide; c, propionamide; d, ethoxyacetamide; e, monochloroacetamide; f, formamide; g, dichloroacetamide; h, trichloroacetamide; and i, trifluoroacetamide.

There are many possible sources for error involved in the determination of the absolute intensities. Among these are the

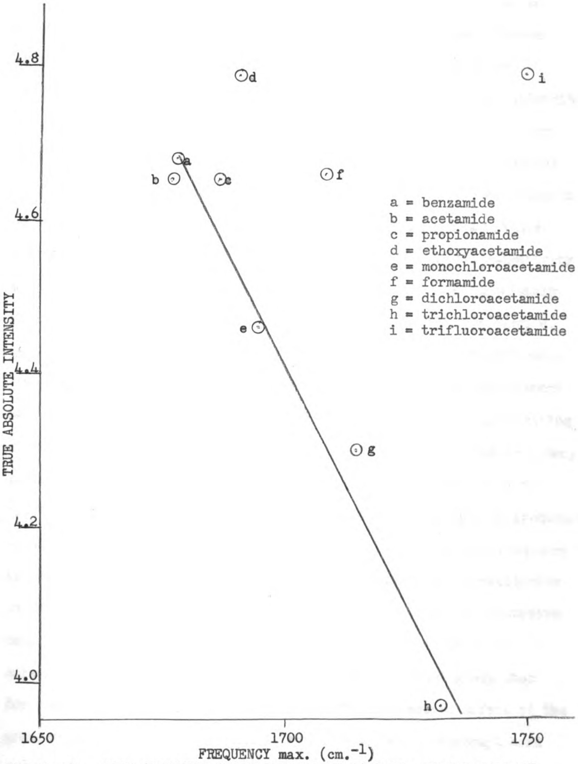


FIGURE II. TRUE ABSOLUTE INTENSITY VERSUS CARBONYL PEAK FREQUENCY FOR A SERIES OF AMIDES frequency and intensity reproducability of the spectrometer, the amount of scattered light present, weighing errors, losses due to evaporation, purity of the compounds, uniformity and determination of the cell thickness, and the noise level of the spectrometer. In consideration of these possible errors the accuracy of the intensity values can only be assumed to be good within plus or minus five per cent. The relationship between the absolute intensity and frequency is reasonably good with the exception of formamide, trifluoroacetamide and ethoxyacetamide. These are the same three compounds which did not follow the linear relationship between effective electronegativity and frequency. It is felt that the mass effect discussed previously shifts the carbonyl vibration of formamide to a higher frequency, u, causing it to be out of order in the frequency intensity relationship. However, no plausible explanation can be offered for the disagreement of the ethoxyacetamide. Trifluoroacetamide shows a rather interesting divergence from the linear relationship described above. Its frequency is high as would be expected from the large inductive effect of the trifluoromethyl group. However, an examination of the plot of frequency versus effective electronegativity, Figure I, shows that the frequency is not as high as would be expected. In fact, the trifluoroacetamide has the highest intensity of any of the amides; whereas, the opposite would be expected. It is possible that another component of the normal vibration is much larger for the trifluoromethyl group than for any group in the other amides. The strong inductive effect of the group will produce a much larger dipole normal to the carbonyl bond axis than any of the other groups. For this case a bending motion of the groups attached to the carbonyl group, even though not a large component of the normal vibration, may make a relatively much larger contribution to the intensity due to a change in this dipole. Bayliss (36) observed that in dipolar solvents such as chloroform the intensity values of certain ketones were greatly increased above what would be expected from a consideration of the refractive index of the solvent. It was claimed that in polar solvents such as chloroform there are two superimposed effects; an electronic component and an orientation component for which no simple theory exists.

Considering all factors it appears that there is a linear relationship between frequency and intensity for the amides investigated. The majority of the amides can exert only an inductive effect with the exception of benzamide. In benzamide the benzene ring is conjugated with the carbonyl group but nevertheless it is in good agreement with the frequency intensity relationship indicating that conjugation with another group does not invalidate the linear relationship of frequency and intensity. However, there are instances in the literature where other effects appear to be operative. Wulf (37) reported that in the ortho halogenated phenols the frequency of the hydroxyl group decreased as the intensity decreased. That is, ortho iodophenol has the lowest frequency and the lowest intensity whereas ortho fluorophenol has the highest intensity and highest frequency. There is, at the present time, no plausible explanation for this effect.

The shape of the curves of Figures III to XV which represent the plot of $\log_e I_0/I$ versus frequency for the amides show an interesting relationship. The symmetrical curves are those for formamide, benzamide, trichloroacetamide and trifluoroacetamide. The remaining curves show either a splitting at the peak, a shoulder on the curve or two distinct peaks. In discussing these it is important to consider the proximity of the substituent groups to the carbonyl. Construction of the Hirshberg models of the amides showed clearly that with the exceptions of formamide, trifluoroacetamide, acetamide and benzamide steric effects were present. Repulsion between non bonding electrons will result in field effects and hindered rotations. The low frequencies and high intensities of the amides with respect to the esters and acids indicate a much larger contribution of the charge separated canonical form (b)

(b) (a)

for the amides. It would be expected then that the group A will have an effect on the shape of the carbonyl absorption curve due to the existence of a plane of resonance for the amide forms (a) and (b). From the models of the compounds it could be observed that steric inhibition to the rotation of group A can exist. These effects of group A would result in restricted rotation of the group giving rise to certain favored rotational positions of group A with respect to the resonance plane of the amide. For a group A which is symmetrical these effects would not manifest themselves in the absorption curve. For example, trichloroacetamide shows a steric repulsion but its absorption curve is symmetrical. For the cases where there is no steric effect as in formamide, acetamide, benzamide and trifluoroacetamide the carbonyl absorption curves should be symmetrical. However, of these acetamide is not symmetrical, and shows two distinct peaks. This has been attributed by Davies (38) to the presence of an equilibrium between unassociated and associated molecules of acetamide in chloroform solution. The more intense peak at 1678 cm.$^{-1}$ is due to the associated form, while the less intense peak at 1702 cm.$^{-1}$ is due to the unassociated form. It was demonstrated by Davies that in very dilute solution the 1702 cm.$^{-1}$ peak becomes the more intense. A plot of the molar extinction coefficient of each peak corrected for absorption due to the adjacent peak versus concentration supports the contention that the relative intensity of the peaks is reversed in very dilute solution.

The remaining amides are all unsymmetrical and show steric inhibition to rotation as a result of which certain rotational positions of group A should be favored leading to an unsymmetrical carbonyl absorption curve. The exact location of these favored positions is at present unknown. As a result of these favored positions of the unsymmetrical amides more than one form of the normal vibration for the carbonyl group exists leading to the dissymmetry of the carbonyl absorption curve. Despite these complicating factors

the relationship between frequency and intensity of the carbonyl band seem to depend, in the main, on the inductive effect of the substituent groups.

A very interesting effect is observed when a bromine atom is substituted on the nitrogen atom of mono, di, and trichloroacetamides. The value for B, the apparent integrated intensity, decreases by approximately 0.75 intensity units but the frequency shows no appreciable change. Obviously the N-bromoamides will not show the same linear relationship between frequency and intensity of the amides. However, as a separate group this correlation holds. The intensity frequency relationship cannot be interrelated among different types of compounds such as esters, amides and N-bromoamides. Addition of a bromine atom in the four position of a 3-ketosteroid decreases the intensity by 0.65 units and increases the frequency by 18 cm.$^{-1}$ This is explainable by the inductive effect of the bromine atom. In the case of the amides, however, no such change of frequency is evident and thus an inductive effect in itself cannot explain the results. In fact, no explanation of this can be offered at the present time.

The effect of solvent is worthy of comment. In Table I are summarized the changes in frequency and apparent intensity in changing from carbon tetrachloride to chloroform for those compounds which were studied in both solvents.

TABLE I

VARIATIONS IN FREQUENCY AND APPARENT INTENSITY IN CHANGING FROM CARBON TETRACHLORIDE TO CHLOROFORM AS SOLVENTS

Compound	$\Delta\nu_m$ cm^{-1}	ΔB m^{-1} cm^{-1}
Ethoxyacetamide	-9	0.21
N-Bromomonochloroacetamide	-20	0.25
N-Bromodichloroacetamide	-5	0.45
N-Bromotrichloroacetamide	-15	0.07
Dichloroacetamide	-11	0.29

An examination of Table I shows that no systematic change in frequency is evident. The frequency decreases while the apparent intensity increases in all cases. However, the intensity change for the trichloroacetamide is quite small. These changes in frequency and intensity can qualitatively be related to changes in the refractive index and dielectric constant of the medium (36). There is also considerable evidence that chloroform is capable of hydrogen bonding with polar groups such as the carbonyl group (39,40). Such effects would be expected to lead to an increased intensity and decreased frequency. The small change in intensity for the N-bromotrichloroacetamide could be related to a steric inhibition to hydrogen bonding with the chloroform solvent.

The main object of the present work was to relate some physical property of the N-bromo compounds or their parent amides to their chemical behavior as brominating agents. From the intensity versus frequency relationship which was explained on the basis of the relative inductive effects of substituent groups it can be concluded that the larger the inductive effect of the substituent group the more ionic in character is the nitrogen to bromine bond. That is, the bromine atom increases in positive character with increasing inductive effect. A good deal more data will be needed to investigate the possibility of other effects being present which may influence the mechanism of the bromination reaction, with N-bromoamides.

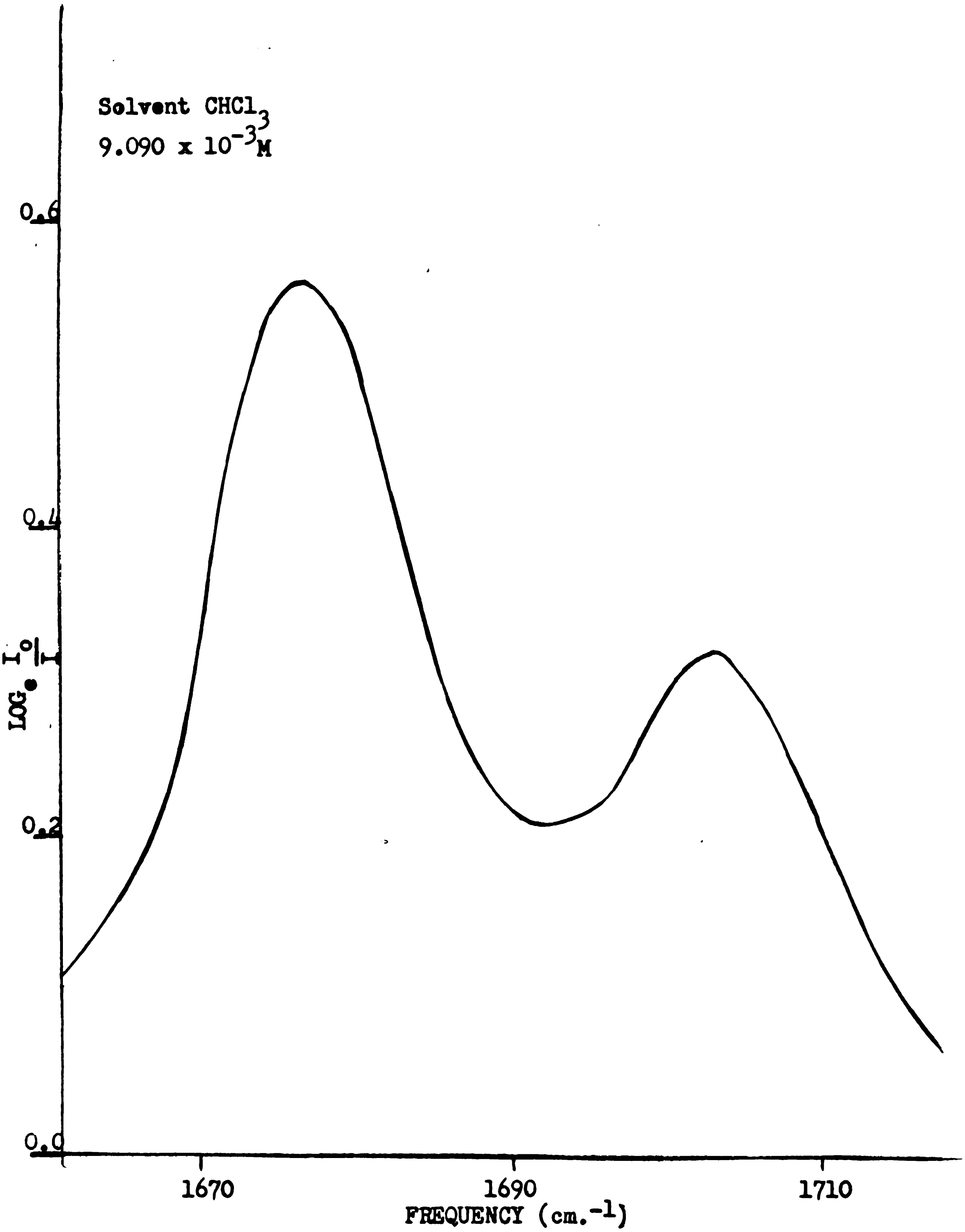


FIGURE III. CARBONYL ABSORPTION BAND FOR ACETAMIDE (INFRARED)

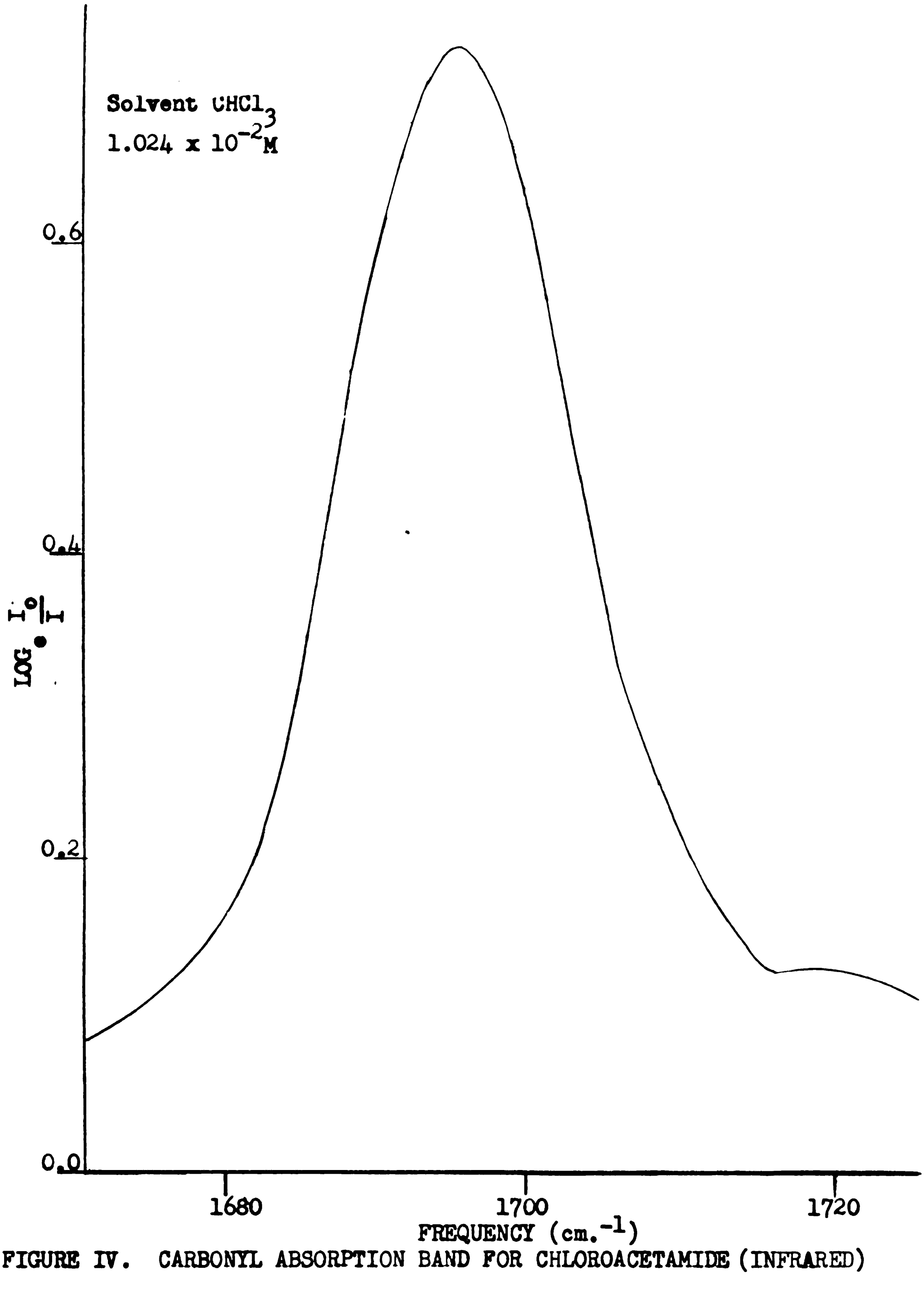


FIGURE IV. CARBONYL ABSORPTION BAND FOR CHLOROACETAMIDE (INFRARED)

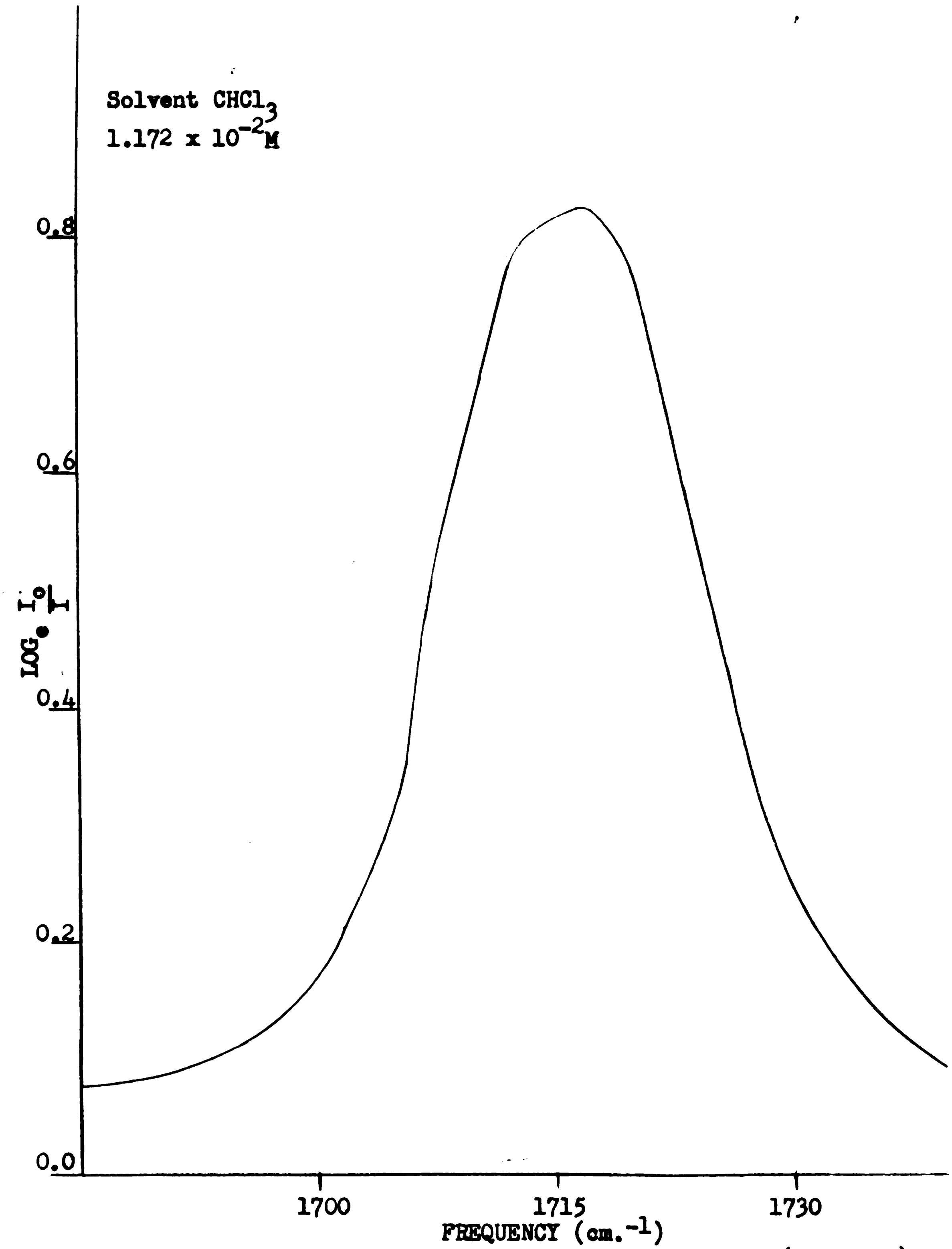


FIGURE V. CARBONYL ABSORPTION BAND FOR DICHLOROACETAMIDE (INFRARED)

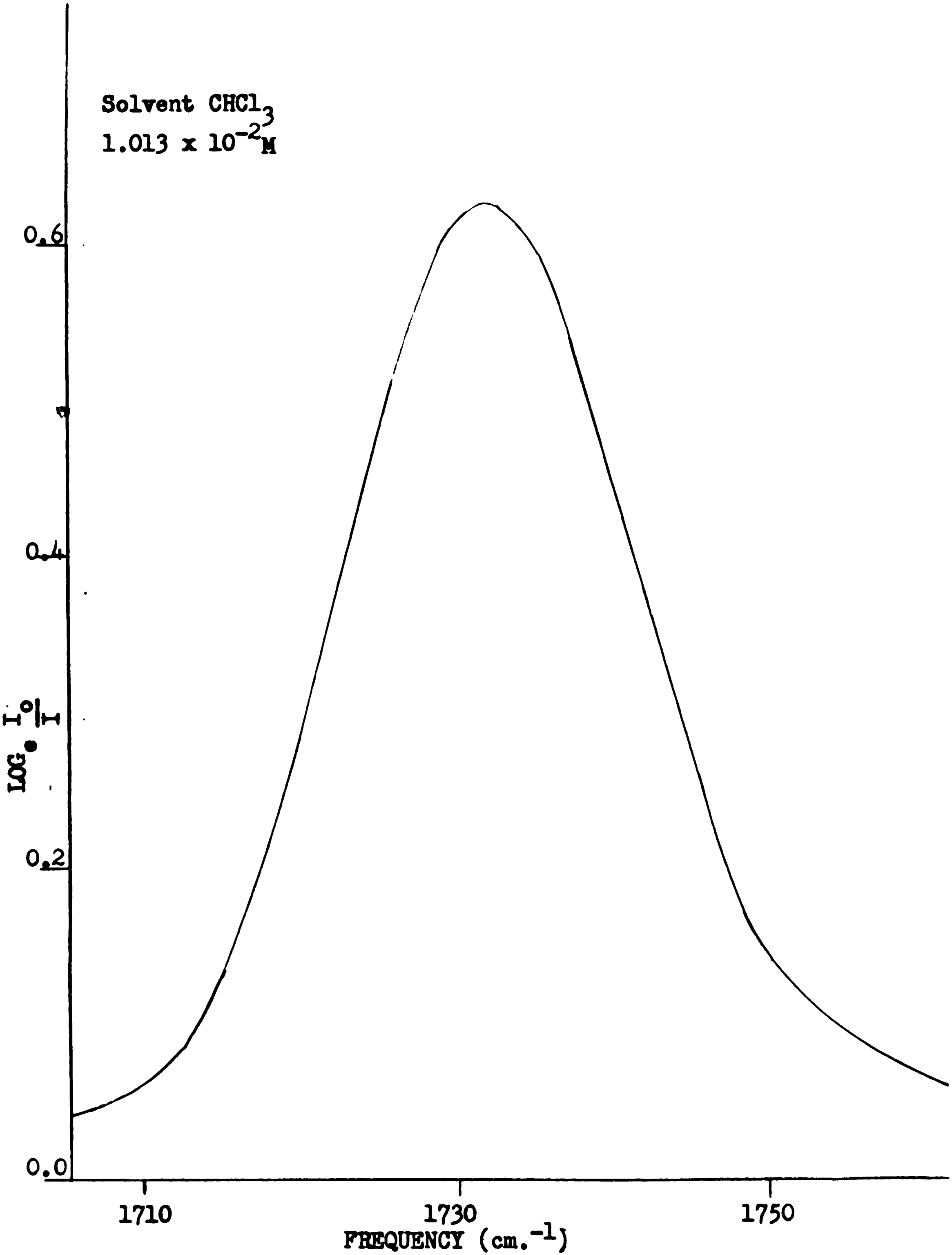


FIGURE VI. CARBONYL ABSORPTION BAND FOR TRICHLOROACETAMIDE (INFRARED)

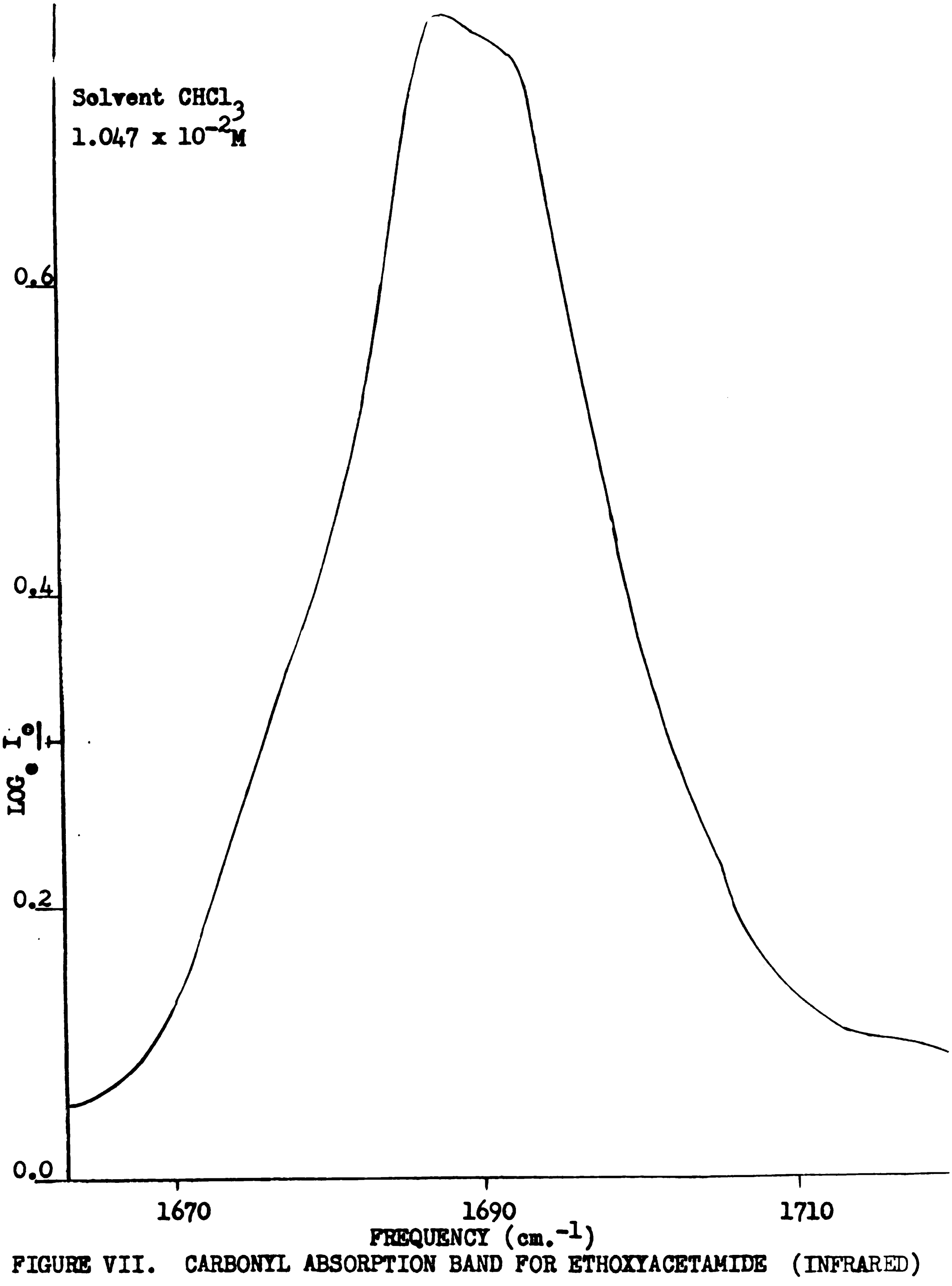


FIGURE VII. CARBONYL ABSORPTION BAND FOR ETHOXYACETAMIDE (INFRARED)

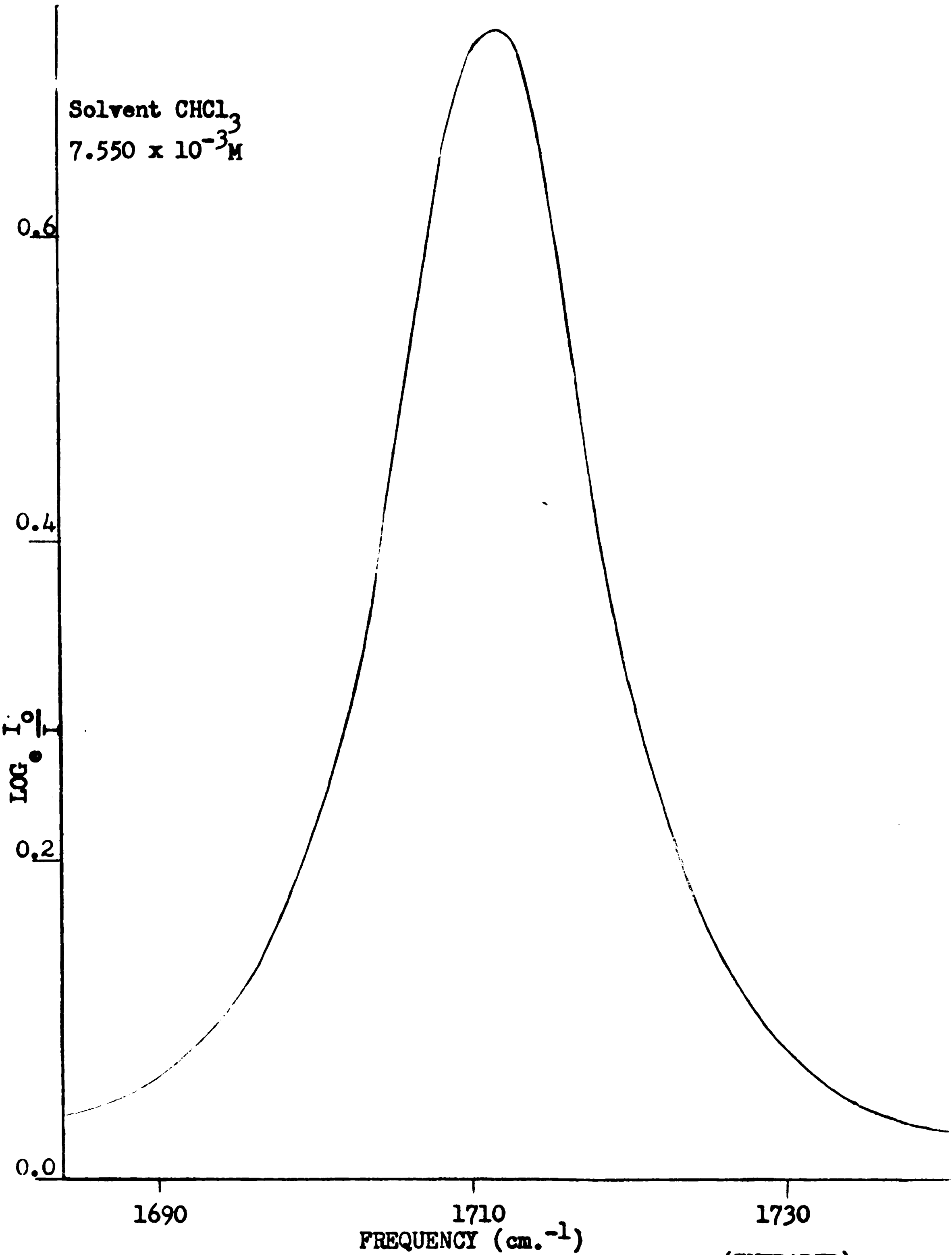


FIGURE VIII. CARBONYL ABSORPTION BAND FOR FORMAMIDE (INFRARED)

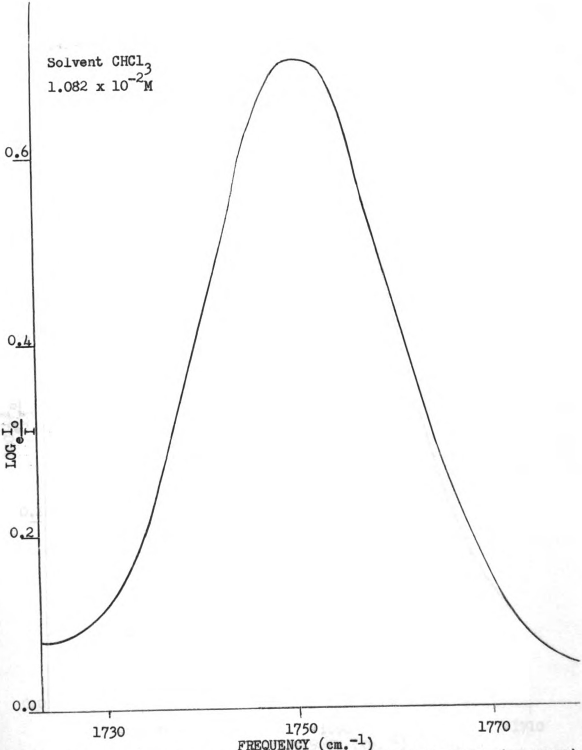


FIGURE IX. CARBONYL ABSORPTION BAND FOR TRIFLUOROACETAMIDE (INFRARED)

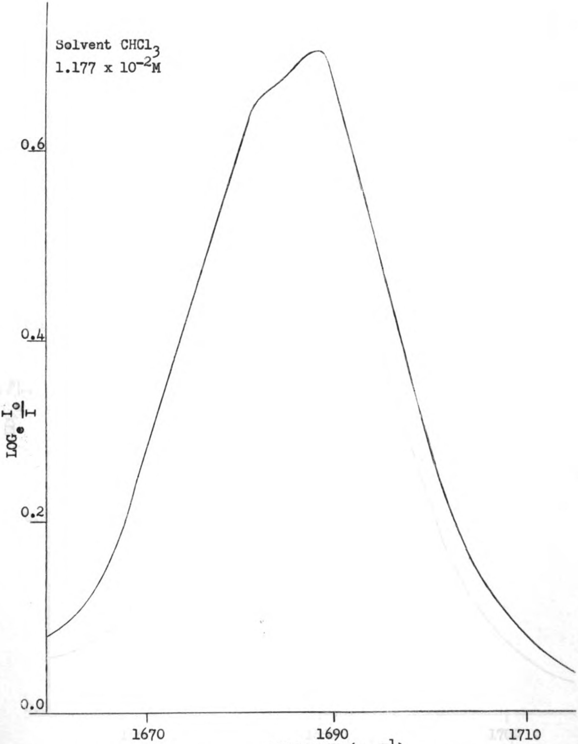


FIGURE X. CARBONYL ABSORPTION BAND FOR PROPIONAMIDE (INFRARED)

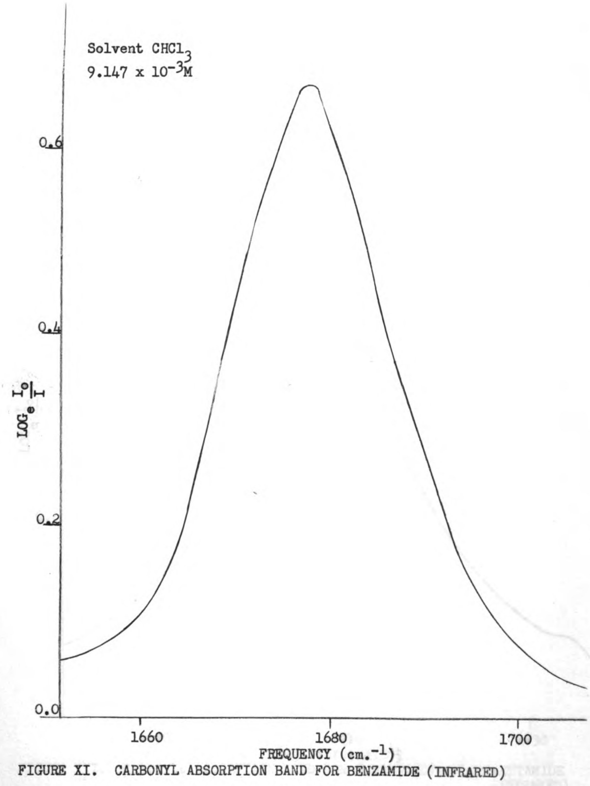


FIGURE XI. CARBONYL ABSORPTION BAND FOR BENZAMIDE (INFRARED)

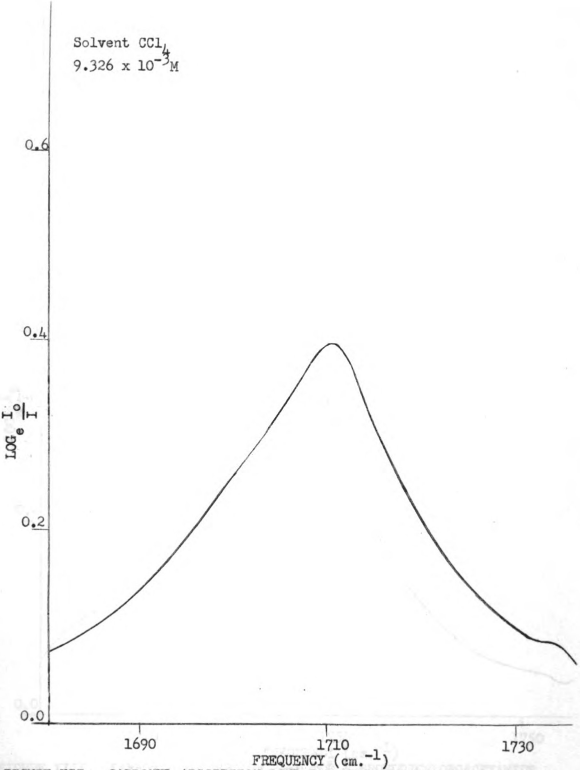


FIGURE XII. CARBONYL ABSORPTION BAND FOR N-BROMOMONOCHLOROACETAMIDE (INFRARED)

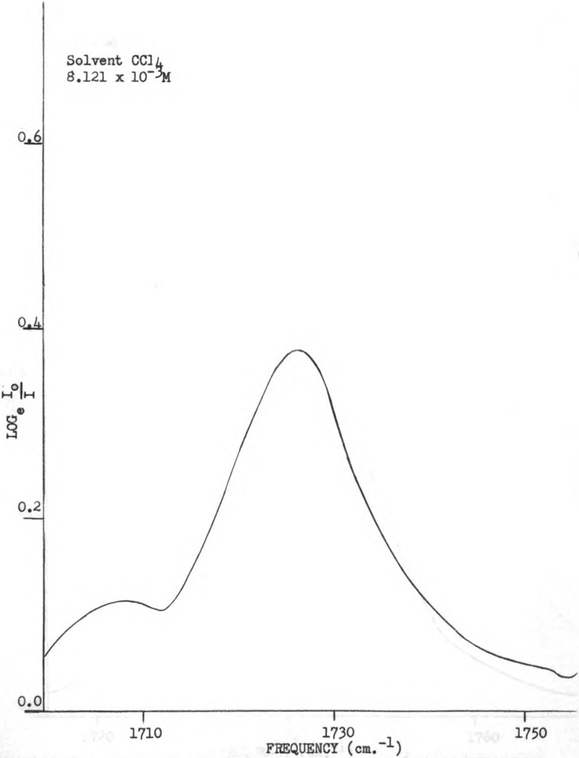


FIGURE XIII. CARBONYL ABSORPTION BAND FOR N-BROMODICHLOROACETAMIDE (INFRARED)

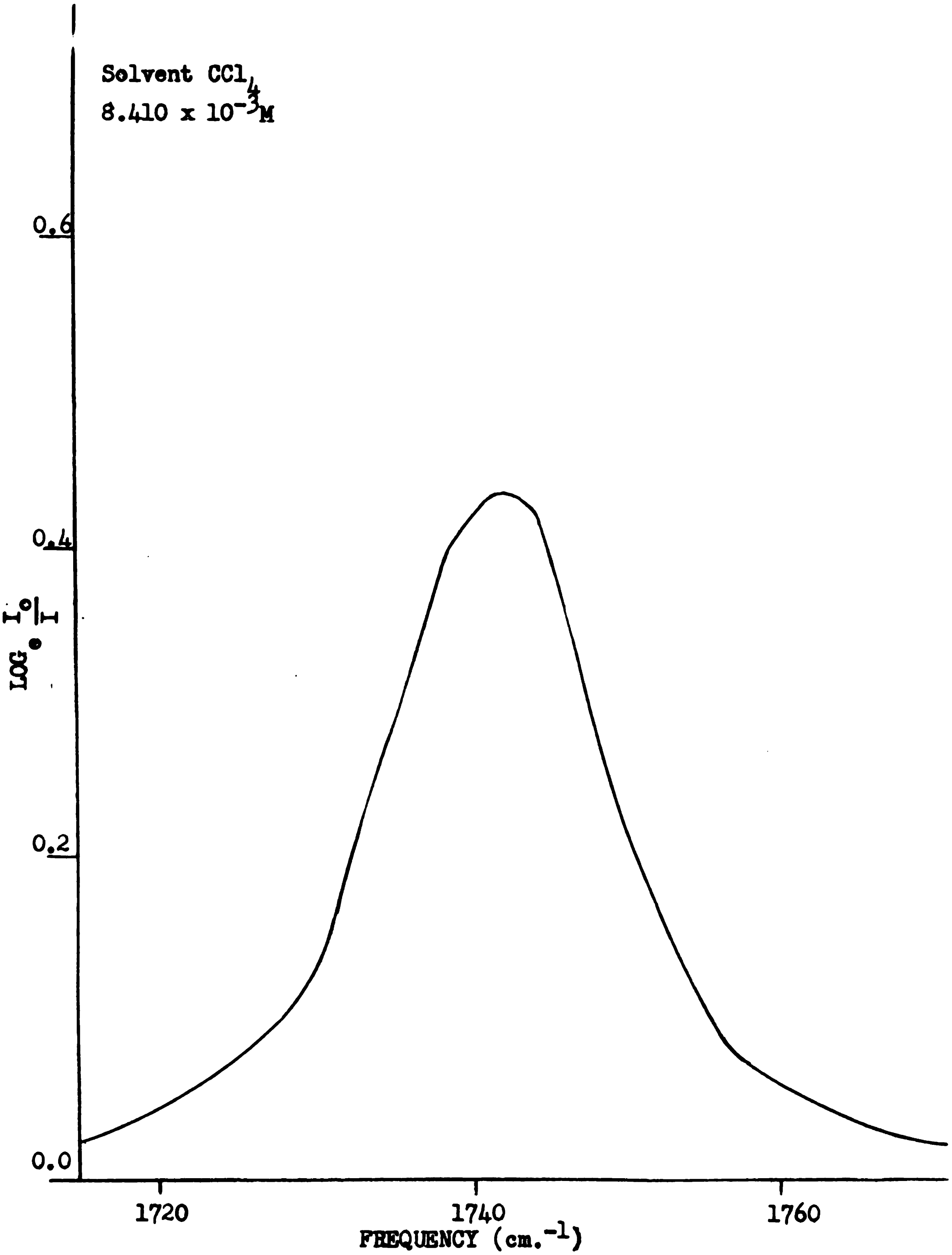
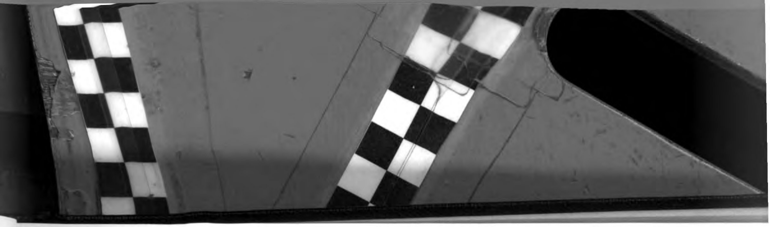


FIGURE XIV. CARBONYL ABSORPTION BAND FOR N-BROMOTRICHLOROACETAMIDE (INFRARED)



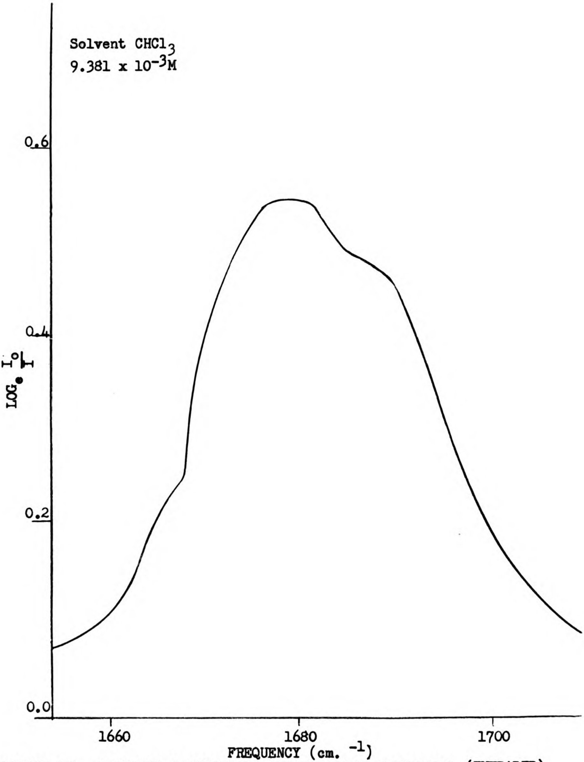


FIGURE XV. CARBONYL ABSORPTION BAND FOR PHENYLACETAMIDE (INFRARED)

EXPERIMENTAL

EXPERIMENTAL

Equipment

The carbonyl absorption band for each of the compounds investigated was determined employing a Perkin Elmer model 21 double beam infrared spectrometer equipped with a sodium chloride optical system. A fixed slit width of 30 microns was employed resulting in a spectral slit width of approximately 3.5 cm^{-1}. The sample cell used had a thickness of 0.487 cm., as determined by the interference fringe method, initially developed by Smith and Miller (19) and later modified by Sutherland and Willis (20). In using the interference fringe method the infrared transmission of the empty cell is determined over a spectral region where clearly distinguishable maxima and minima result due to interference between reflected and transmitted beams within the cell. These maxima and minima are numbered serially and the serial numbers are plotted, as coordinate, against the wave numbers in $cm.^{-1}$ of the maxima and minima as abscissa. Such a plot gave a straight line having a slope of 4t where t is the cell thickness in cm.

The Perkin Elmer spectrometer was operated initially with the solvent contained in the reference cell. However, it was later found that in a region where the solvent showed absorption that the presence of solute in the sample cell depressed the absorption due to solvent by an amount greater than was expected from a consideration of the mole fraction of the solvent in the solution of the compound being investigated.

In order to correct for this phenomenon the spectrometer was operated with both beams open and employing no reference cell interposed in the reference beam. Atmospheric water bands were utilized as reference for frequency calibration. A base line of 90 per cent transmission was used in all of the determinations.

Materials

Chloroform was the solvent used for the determination of the infrared spectra of all the compounds studied. In addition, with certain compounds, where their solubility permitted, carbon tetrachloride was used as a solvent in order to investigate effects on the spectra due to the solvent. In this investigation the use of both reagent grade and spectrophotometric grade solvents resulted in identical data within experimental error.

Acetamide, benzamide and formamide were obtained from Eastman Organic Chemicals. Formamide was freshly distilled each time just before it was used. Acetamide and benzamide were recrystallized respectively from chloroform and water followed by drying in a vacuum dessicator just prior to each time they were used. The preparations of the N-bromo mono, di, and trichloroacetamides are described in the second part of this thesis. They were recrystallized from carbon tetrachloride, dried in the absence of any light under vacuum and analyzed (21) for bromine immediately before being used.

All melting points and boiling points are in °C and are uncorrected.

Preparation of Phenylacetamide (22)

In a one liter single neck flask, fitted with a 30 cm. vigreux column and distillation head, were placed 136 g., 1.0 mole and 120 g., 1.05 moles of ammonium carbonate followed by the addition of 200 ml., 3.5 moles, of glacial acetic acid. The reaction mixture was gradually heated until all the materials boiling below 150°C. had distilled. The maximum rate of distillation was not allowed to exceed 100 milliliters an hour. The residue from the reaction mixture, containing the crude product was poured, while still hot, into twice its volume of water and neutralized with dilute ammonium hydroxide to a phenolphthalein end point. The phenylacetamide was recovered by filtration, recrystallized from water and dried at 105°C. for two hours. The amount of product obtained was 85 g., 0.63 mole, and 63 per cent yield. Its melting point was 157-157.2°C. and that reported (22) for the same material is 157°C.

Preparation of Propionamide (23)

Into a half liter single neck flask equipped with a 30 cm. vigreux column and distillation head were placed 120 g., 1.05 moles, of ammonium carbonate and 145 g., 1.95 moles, of propionic acid. The temperature of the reaction mixture was gradually raised until all the material boiling below 200°C. had been distilled at a rate of distillation not in excess of 100 ml. per hour. The crude product remaining in the distilling flask solidified on cooling and was recrystallized from benzene followed by drying in a vacuum dessicator over paraffin wax. The amount of product obtained was 93 g., 1.27 moles, a 65 per cent yield. Its melting point was 81.3-81.5°C. and that reported (23) for the same material is 81.0°C.

Preparation of Trifluoroacetamide (24)

Into a half liter two neck flask, the quantities, 144 g., 1.26 moles, of trifluoroacetic acid and 14.2 g., 0.1 mole, of anhydrous sodium sulfate were placed. To this a mixture of 178 ml., 3.05 moles, of absolute ethanol and 55 ml., 1.03 moles, of concentrated sulfuric acid was added slowly which caused sufficient evolution of heat so that the reaction mixture had to be cooled. Following the addition of the alcohol acid mixture the reaction mixture was set aside for nine hours and then distilled on a steam bath. The fraction boiling in the range 55-56°C. was collected, washed with 100 ml. of cold 5 per cent sodium carbonate and dried over 25 g. of calcium chloride at 0°C. This crude product was then redistilled from phosphorous pentoxide and the fraction boiling in the range 61-61.5°C. was collected, dissolved in 100 ml. of anhydrous ethyl ether and then ammonia gas was bubbled rapidly through this solution until no further precipitation of product was observed. The solid was filtered, recrystallised from ethyl ether and dried by means of a vacuum pump to give a 70 per cent yield of pure product with a melting point of 73-74°C. Its reported melting point is 75°C. (24).

Preparation of Ethoxyacetamide (26)

In a one liter three neck flask fitted with a stirrer, reflux condenser and dropping funnel were placed one liter, 17.1 moles, of absolute ethanol to which was added 46 g., 2.0 moles, of metallic sodium in small portions. When all of the sodium had reacted the stirred reaction mixture was supported in an ice bath and 223 g., 1.82 moles, of crude ethyl chloroacetate was added dropwise over a two hour period. Stirring of the reaction mixture was continued for an additional four hours following the addition of the haloester after which the sodium chloride was removed by filtration. The sodium chloride was washed with several small portions of ether which were combined with the filtrate. Following removal of the ether and alcohol on a steam bath the residue was fractionally distilled and the product boiling at 152-153°C. was collected. The product, ethyl ethoxyacetate, was added in moderate portions to a well stirred 200 ml. quantity of concentrated ammonium hydroxide, through which ammonia gas was being passed. When the exothermic reaction had ceased the precipitate was filtered, recrystallized from benzene and dried in a vacuum dessicator over strips of paraffin wax. The quantity of pure amide obtained was 93.8 g., 0.91 mole, a 50 per cent yield based on the ethyl chloroacetate. The amide melted at 80.8-82.0°C. The reported melting point for this compound is 80-82°C. (27).

Preparation of Chloroacetamide (28)

Into a half liter single neck flask, were placed 85 g., 0.89 mole, of chloroacetic acid and 138 g., 3.00 moles, of absolute ethanol. The mixture was refluxed for two hours after which it was slowly distilled and the ethyl chloroacetate boiling in the range 143-144°C. was collected. The chloroester was added to 150 ml. of concentrated ammonium hydroxide and was shaken until no further precipitation occurred. The solid amide was filtered, recrystallized from water and dried by heating under vacuum for several hours. The weight of amide was 42 g., 0.45 mole, and corresponded to a 50 per cent yield based on the chloroacetic acid. It melted at 119-120°C. The reported melting point for this compound is 119-120°C. (28).

The dichloroacetamide and the trichloroacetamide were prepared from the corresponding dichloro and trichloroacetic acids by employing exactly the same experimental procedure as that previously described for chloroacetamide.

The dichloroacetamide was obtained in a 25 per cent yield after recrystallization first from water and then from benzene. The reported melting point for the material is 98°C. while that observed for the product prepared in this work was 97.5-98°C.

The trichloroacetamide was obtained in a 70 per cent yield from the acid after a single recrystallization from water. It had a melting point of 139-139.5°C., while that reported for the same compound is 140-141°C.

Experimental Conditions

It should be noted that the infrared absorption data obtained were independent of the solvent used for the recrystallization of the several amides. That is, while for a given amide different solvents were used for its recrystallization just prior to use, the infrared absorption results were not affected.

The amide samples were recrystallized, dried, weighed out and immediately transferred to a volumetric flask and dissolved in chloroform or carbon tetrachloride.

The sample cell was then rinsed several times with the solvent being used, after which it was filled with the same solvent. The cell was then placed in the sample beam and the base line was adjusted to 90 per cent transmission. The per cent transmission of the solvent was measured over a range of sufficient breadth to include an area 50 cm.$^{-1}$ on either side of the carbonyl band maximum of the amide being investigated. The wave length of the light source was controlled manually in such a manner that the pointer would come to equilibrium and an accurate reading of the per cent transmission could be made. Readings of per cent transmission were taken every 0.01 micron over this range. This procedure was then repeated for the amide solution, the per cent transmission and wave length were recorded, utilizing a base line set at 90 per cent transmission. From the per cent transmission readings the value of $\log_e I_o/I$ was calculated for both the solvent and the solution. The value of $\log_e I_o/I$ for the solvent was subtracted from the value of $\log_e I_o/I$ for the solution at each reading to give the net value of $\log_e I_o/I$ due to the carbonyl group of the amide or N-bromoamide.

A typical set of infrared absorption data, for formamide, is shown in Table II. The similar data for the other amides and the N-bromoamides investigated in the present study are in an appendix at the end of the second part of this thesis, Tables XIII to XXVI.

Method of Obtaining Absolute Intensity

The net value of $\log_e I_0/I$ due solely to the carbonyl group of the amide was plotted against the frequency in wave numbers. A distance of 50 cm.$^{-1}$ was marked off on each side of the carbonyl band maximum. The area under the curve of the carbonyl absorption band was then determined by cutting out the curve to a distance of 50 cm.$^{-1}$ on each side of the band maximum and comparing its weight to the weight of the same paper of known area. However, it was found that both more accurate and reproducable results were obtained for the area determination under absorption bands by using an "Ott" compensating planimeter and consequently it was employed in such area determinations for the majority of the absorption curves.

The integrated absorption intensity of each amide and its N-bromoamide derivative was calculated from the areas obtained by the above method. However, due to the use of a finite slit of 30 microns in the present work the radiation was not monochromatic in character resulting in values for the absorption intensity, calculated from the areas under the absorption curve representing only the apparent integrated absorption intensity, B. Its value is given by the equation,

TABLE II

INFRARED ABSORPTION DATA FOR FORMAMIDE

Solvent $CHCl_3$-0.01133M, Base Line 90 Per Cent of Transmission

Wave Length		Solvent		Solution		Net Carbonyl
u	$\bar{\nu}$	%T	$\log_e I_0/I$ 10^3	%T	$\log_e I_0/I$ 10^3	$\log_e I_0/I$ 10^3
5.680	1761	89	11	87.5	28	17
5.690	1757	89	11	87	33	22
5.700	1754	89	11	86.5	30	29
5.710	1751	89	11	86	46	35
5.720	1748	89	11	86.5	40	29
5.730	1745	89	11	86	46	35
5.740	1742	89	11	86	46	35
5.750	1739	89	11	85.5	52	41
5.750	1736	89	11	84	69	58
5.770	1733	89	11	83	80	69
5.780	1730	89	11	80	117	106
5.790	1727	89	11	76	168	157
5.800	1724	89	11	71	237	226
5.810	1721	88	22	63	357	335
5.820	1718	88	22	55	494	472
5.830	1715	89	11	41	786	775
5.840	1712	89	11	32	1035	1024
5.850	1709	89	11	30	1099	1088
5.860	1706	89	11	36	916	905
5.870	1704	89	11	43	738	727
5.880	1701	89	11	56	474	463
5.890	1698	89	11	65	325	314
5.900	1695	89	11	72.5	216	205
5.910	1692	89	11	76	168	157
5.920	1689	89	11	78	142	131
5.930	1686	89	11	79	130	119
5.940	1684	89.5	6	84	69	63
5.956	1681	89	11	84	69	58
5.960	1678	88.5	17	84	69	52
5.970	1675	89.5	6	84	69	63
5.980	1672	89.5	6	84	69	63
5.990	1669	89.5	6	86.5	40	34
6.000	1667	89.5	6	86.5	40	34
6.010	1664	89.5	6	86.5	40	34
6.020	1661	89.5	6	86.5	40	34
6.030	1658	89	11	86.5	40	29

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$$B = \frac{1}{Cl} \int \log_e (T_0/T)_\nu \, d\nu$$

where C is the concentration in moles per liter, l is the path length in centimeters, T_0 and T are the incident and transmitted radiation when the spectrometer is set at a frequency of ν (29).

The results of the calculations are listed in Table III.

The corrections which must be applied to B, the apparent integrated adsorption intensity, in order to obtain the true integrated absorption intensity, A, have been discussed by Ramsay (29).

The method employed to convert B to A depends on the band shape, the relation of the slit function to the extent of the wing correction, and the slope of the extrapolation. Since no concentration effect was discernible for any of the compounds in the concentration range employed in the present investigation no extrapolation to zero concentration or path length was necessary. The values obtained for the apparent integrated absorption intensity, B, differ from the true value, A, by the so-called "wing" correction. If the band is considered to extend indefinitely the residual area under the "wings" may be an appreciable fraction of the total area of the band, for while the absorption is small the frequency interval by which it is multiplied is very large. This "wing" correction was applied by dividing the frequency range 50 cm.$^{-1}$ on both sides of the band center by one half of the band width at half intensity. Table IV shows the corrections which were applied to the apparent integrated absorption intensities, B, to get the true value of the integrated absorption intensities, A.

TABLE III

APPARENT INTEGRATED ABSORPTION INTENSITIES FOR SOME AMIDES AND THEIR N-BROMO DERIVATIVES

Compound	Frequency $V_{max}(cm^{-1})$	Concentration Moles/liter	Apparent Integrated Intensity $B, lm^{-1} cm^{-2}$	Average Value of B
Acetamide	1677,1702	0.00992	4.28×10^4	$4.21\times10^4\pm0.03$
	1678,1703	0.00909	4.21×10^4	
	1678,1703	0.00930	4.21×10^4	
	1677,1702	0.01419	4.16×10^4	
Chloroacetamide	1696	0.01106	3.92×10^4	
	1695	0.01024	3.95×10^4	$3.95\times10^4\pm0.02$
	1695	0.01783	3.97×10^4	
Dichloroacetamide	1717	0.01172	3.79×10^4	
	1715	0.01011	3.73×10^4	$3.76\pm10^4\pm0.02$
	1714	0.01530	3.77×10^4	
Trichloroacetamide	1732	0.01485	3.37×10^4	
	1733	0.00743	3.35×10^4	$3.37\times10^4\pm0.02$
	1730	0.01032	3.41×10^4	
	1731	0.00869	3.36×10^4	
Ethoxyacetamide	1691	0.01388	4.19×10^4	
	1691	0.01157	4.21×10^4	$4.19\times10^4\pm0.01$
	1690	0.01455	4.18×10^4	
Ethoxyacetamide in CCl_4	1698	0.01437	3.94×10^4	
	1699	0.00719	4.00×10^4	$3.98\times10^4\pm0.03$
	1699	0.01524	4.01×10^4	
	1700	0.01455	3.96×10^4	
Formamide	1709	0.01133	4.20×10^4	
	1709	0.00755	4.24×10^4	$4.22\times10^4\pm0.01$
	1710	0.00945	4.22×10^4	
Trifluoroacetamide	1749	0.01627	4.02×10^4	
	1751	0.00814	4.01×10^4	$4.04\times10^4\pm0.01$
	1750	0.00515	4.06×10^4	
	1750	0.01082	4.05×10^4	
Propionamide	1688	0.00896	3.89×10^4	
	1687	0.01177	3.84×10^4	$3.85\times10^4\pm0.03$
	1687	0.01338	3.83×10^4	

Continued

TABLE III - Continued

Compound	Frequency ν_{max}(cm^{-1})	Concentration Moles/liter	Apparent Integrated Intensity B, l m^{-1} cm^{-2}	Average Value of B
Phenylacetamide	1679	0.01020	4.47x10^4	4.48x10^4±0.03
	1679	0.00510	4.53x10^4	
	1679	0.01099	4.45x10^4	
Benzamide	1678	0.00835	4.02x10^4	4.06x10^4±0.02
	1678	0.00418	4.09x10^4	
	1679	0.00763	4.06x10^4	
Dichloroacetamide in CCl_4	1726	0.00835	3.47x10^4	3.47x10^4
N-Bromomonochloroacetamide	1690	0.01096	3.22x10^4	3.19x10^4±0.02
	1692	0.00548	3.20x10^4	
	1692	0.01242	3.15x10^4	
N-Bromomonochloroacetamide in CCl_4	1711	0.00948	2.96x10^4	2.94x10^4±0.03
	1712	0.00933	2.96x10^4	
	1712	0.00866	2.88x10^4	
N-Bromodichloroacetamide	1718	0.01069	3.14x10^4	3.14x10^4
N-Bromodichloroacetamide in CCl_4	1725	0.00822	2.69x10^4	2.69x10^4
N-Bromotrichloroacetamide	1728	0.01077	2.59x10^4	2.61x10^4±0.02
	1728	0.00539	2.58x10^4	
	1727	0.00898	2.63x10^4	
	1726	0.00449	2.62x10^4	
	1728	0.01007	2.64x10^4	
N-Bromotrichloroacetamide in CCl_4	1742	0.00820	2.58x10^4	2.55x10^4±0.02
	1744	0.00971	2.52x10^4	
	1743	0.00789	2.55x10^4	

TABLE IV

TRUE INTEGRATED ABSORPTION INTENSITIES FOR SOME AMIDES AND THEIR N-BROMO DERIVATIVES

Compound	Bx10^4 lm.$^{-1}$ cm.$^{-2}$	Δ V$_{\frac{1}{2}}$ cm.$^{-1}$	Correction Per Cent	A x 10^4 lm.$^{-1}$ cm.$^{-2}$	Solvent
Acetamide	4.21		10.0	4.63	$CHCl_3$
Chloroacetamide	3.95	18	12.8	4.46	$CHCl_3$
Dichloroacetamide	3.76	20	14.4	4.30	$CHCl_3$
Trichloroacetamide	3.37	24	17.5	3.96	$CHCl_3$
Ethoxyacetamide	4.19	20	14.4	4.79	$CHCl_3$
Ethoxyacetamide	3.98	22	16.0	4.62	CCl_4
Formamide	4.22	15	10.5	4.66	$CHCl_3$
Trifluoroacetamide	4.04	25	18.5	4.79	$CHCl_3$
Propionamide	3.85	26.8	20.2	4.63	$CHCl_3$
Benzamide	4.06	21	15.2	4.68	$CHCl_3$
Dichloroacetamide	3.47	18	12.8	3.91	CCl_4
Phenylacetamide	4.48				$CHCl_3$
N-Bromomonochloroacetamide	2.94	26	19.4	3.51	CCl_4
N-Bromodichloroacetamide	2.69	17	12.0	3.15	CCl_4
N-Bromotrichloroacetamide	2.55	17	12.0	2.99	CCl_4

Due to the nature of the acetamide curve a correction of ten per cent was applied, which is the average correction indicated by the work of Ramsay (29) for the frequency range covered in the investigation of this compound in the present work. The value of B for phenylacetamide was not corrected since the shape of its absorption curve suggested there was additional absorption besides that due to the carbonyl group. The values of B for the chloroform solutions of the N-Bromo derivatives of mono, di, and trichloroacetamide were not corrected as a consequence of the breadth of these absorption bands and the tendency for these compounds to liberate free bromine in their chloroform solution.

The curves obtained from the plots of $\log_e I_0/I$ versus frequency for the several amides and their corresponding N-bromo derivatives studied in this investigation are shown in Figures III to XV.

SUMMARY

SUMMARY

The absolute integrated absorption intensities of a series of amides and N-bromoamides were determined.

The absolute intensity is related linearly to the carbonyl frequency and the effective electronegativity of the substituent groups in the amides and N-bromoamides.

The shape of the carbonyl absorption curve has been discussed in terms of the steric affect of the substituents.

The higher the absolute intensity and the lower the frequency of the carbonyl the less ionic is the nitrogen bromine bond.

PART II

BROMINATION AND DECOMPOSITION REACTIONS OF SOME N-BROMOAMIDES

INTRODUCTION

INTRODUCTION

The Wohl Ziegler reaction is a general method for the introduction of a bromine atom in the allylic position of an olefin, that is

$$\mathrm{RCONHBr} + \mathrm{-CH=CHCH_2}^{-} \longrightarrow \mathrm{-CH=CHCHBr}^{-} + \mathrm{RCONH_2},$$

by the use of an N-bromoamide or imide under anhydrous conditions.

Wohl (41,42) in 1921 investigated the reactions of N-bromoacetamide with olefins under cold, anhydrous conditions. However, from 1921 to 1941 only a few (2,43,44) additional reports on the use of N-bromoacetamide appeared in the literature. It was not until 1942 that the generality of this reaction was pointed out by Ziegler (45) and his collaborators. They reported on a detailed empirical study which indicated that N-bromosuccinimide was the best available brominating agent. They further reported that N-bromophthalimide which had already been examined by Wohl (42) was fairly satisfactory while such compounds as N-bromoglutarimide and N-bromohexahydrophthalimide were not very useful in this type of reaction.

Since that time the Wohl Ziegler reaction has been widely employed by organic chemists. The discovery of the catalytic effect of peroxides (46), which made possible the bromination of carbonyl compounds and alkyl chains attached to aryl groups, broadened still further the scope of the reaction. The wide interest in the

N-bromoamides and imides has been occasioned by both their paradoxically clean cut specificity and diverse reactivity. Thus under mild but different conditions the N-bromoamides and imides react to substitute bromine in the allyl position (45) or to add hypobromous acid (47,48) or bromine (49,50) across the double bond.

Steroid chemists (51,52,53) in particular have utilized the N-bromoamides and imides. Schmidt (54) and Karrer employed the reaction for the bromination of polyolefins, cyclic ketones and the side chain bromination of alkyl aromatic hydrocarbons. In addition to their varied but specific reactions as brominating agents the N-bromoamides and imides also serve as selective oxidizing agents (55,56) of varying power and specificity.

Buu-Hoi (1) investigated the reaction of N-bromosuccinimide with a wide variety of benzene and naphthalene derivatives, notably ethers, and observed that bromination of both ring and side chain occurred. This dual brominating character of N-bromosuccinimide has more recently been observed in thiophene (2) and in the methyl derivatives of thiophene (3) where both side chain and nuclear brominations have been observed. In many cases, at least, the desired direction of reaction (57) can be controlled by catalysts or conditions.

The fact that the N-bromoamides and imides attack olefins at the same position as reagents generally believed to react through a free radical mechanism strongly suggests such a mechanism for the Wohl Ziegler reaction (58,59,60). However, since nuclear bromination of both aromatic and heterocyclic compounds has been observed (1,2) it is very probable that an ionic mechanism is also operative in this reaction. Thus a plural mechanism is perhaps a better description of the mechanistic processes involved in this reaction, since it is likely that N-bromoamides and imides like N-bromoacetamide and N-bromosuccinimide may react by several mechanisms resulting from homolytic as well as heterolytic dissociation of the reagent. Thus, any acceptable mechanistic concept of the Wohl Ziegler reaction must account for the bromination of olefins in the allylic position, addition of bromine and hypobromous acid to the double bond in alkenes, side chain and ring brominations of aromatic and heterocyclic compounds. Further, it must also account for the abnormal reactions such as vinyl substitution (61) and introduction of the amide or imide nucleus (62) into the product. Finally, any such mechanistic concept should account for the considerable differences in reactivity of such brominating agents as N-bromosuccinimide, N-bromophthalimide, N-bromoglutarimide and N-bromohexahydrophthalimide in the allylic substitution reaction.

The present investigation was undertaken to gain further information concerning the nature of the mechanism of the Wohl Ziegler reaction. A study was made of the effects of structural variation of the brominating agent on the amount of allylic bromination. This was approached by a study of the bromination of toluene, as this material is capable of both side chain and nuclear bromination, under comparable conditions devoid as far as possible from any catalytic effect. Particular emphasis was placed on the development of analytical methods

which would permit a total accounting of all the bromine in the products of the reaction when the original bromine is introduced into the reaction system in the form of the brominating agent.

Both the photo and thermal decompositions of N-bromoamides and imides were briefly investigated since changing sensitivity, due to variations in the structure, of this type of brominating agent, to such decompositions could materially effect the nature of the products in the Wohl Ziegler reaction.

HISTORICAL

HISTORICAL

Several methods for the preparation of N-bromoamides and imides have been described. The method (63) most widely used involves the reaction of the amide with bromine in aqueous alkaline medium. Another method (64) involves the reaction of the amide with bromine and silver oxide in ethylacetate as a solvent. A third method (65) involves the reaction of bromine with the mercury salt of the amide dissolved in chloroform. The method (66) employed in the present work involved the reaction of the amide with silver oxide and bromine in trifluoroacetic acid as a reaction medium.

The bromination of toluene by N-bromoamides and imides has been recorded several times in the literature. Schmidt and Karrer (54) reported that with N-bromosuccinimide a sixty-four per cent yield of benzyl bromide was obtained when benzoyl peroxide was added to the brominating mixture. When aluminum chloride was utilized as the catalyst benzyl bromide was not isolated but a seventy-one per cent yield of a mixture of monobrominated toluenes was realized. In the absence of a catalyst, Schmidt and Karrer reported that bromination did not occur. Buu-Hoi (1) also reported that no bromination occurred without added catalysts. Henne (66) prepared N-bromoperfluorosuccinimide and N-bromoperfluoroglutarimide. When these compounds were allowed to react with toluene, only ring bromination occurred. However, by increasing the reaction temperature to ninety degrees

Centigrade both benzyl bromide and bromo toluenes could be isolated. Park (67) and his co-workers prepared the N-bromo monochloro, dichloro, trichloro, monofluoro, difluoro and trifluoroacetamides and allowed them to react with toluene. These investigators report both ring and side chain bromination and that the ratio of ring to side chain bromination depended on the nature of the brominating agent. The effect of the structure of the brominating agent on the results of the bromination reaction as reported by both Henne (66) and Park (67) was attributed to the electronegativities of the substituents on the α carbons which in turn enhanced the positive character of the bromine atom resulting in nuclear bromination. Park (67) suggested a concerted type of mechanism to describe the side chain bromination of toluene. Bloomfield (60) proposed a free radical mechanism for the allylic bromination and pointed out that allylic rearrangements could be expected in the reaction. The work of Schmidt (54) in which Lewis type acid catalysts were used suggested that nuclear bromination resulted from an ionic mechanism. Recently Bailey and Bello (57) demonstrated the effect of salts coprecipitated with the brominating agent on the mechanism of the bromination reaction. They found that these salts caused an almost exclusive addition of bromine; whereas, added salts did not exert too great an effect. However, if these coprecipitated salts are removed an almost exclusive substitution of bromine occurs.

No investigation of the photochemical or thermal decomposition of the N-bromoamides or imides has been reported in the chemical literature up to the present time.

DISCUSSION

DISCUSSION

The major part of the work carried out in this study was concerned with an investigation into the mechanism of the Wohl Ziegler reaction. The experimental approach followed three main avenues, the examination of the dark reaction of the N-bromoamides with toluene, a study of the infrared spectrum of the N-bromoamides and their parent amides with particular emphasis on the carbonyl band, and an investigation of the photochemical and thermal decomposition of the N-bromoamides.

In the dark reaction of the N-bromoamides with toluene it was hoped to obtain, the length of time for reaction, the total conversion to monobrominated product, the ratio of side chain to ring bromination, and the effect of temperature.

From the infrared spectrum of the N-bromoamides and their parent amides it was hoped to obtain two facts. First, the position of the peaks for the carbonyl band. Secondly, the absolute integrated absorption intensities and to relate these to the quality of the compounds as a brominating agents. This, it was anticipated, would give the effect of variations in structure on the compound as a brominating agent.

The photochemical and thermal decomposition of the N-bromoamides was carried out with three objectives in mind. Initially, to study the relative rates of formation of bromine from which the relative

rates of decomposition of the N-bromoamides could be obtained. Next, to examine the effect of free bromine on these rates of decomposition, and finally to investigate the possibility of complex formation as a step in the mechanism of the bromination reaction.

The minor part of this work was concerned with a study of the comparative reactions of N-bromosuccinimide and N, N'dibromodimethylhydantoin with cyclohexene. These reactions were carried out in carbon tetrachloride and chloroform solvents. In carbon tetrachloride both reagents gave allylic bromination, 3-bromocyclohexene, and polybrominated cyclohexene. The N-bromosuccinimide gave 63 per cent allylic bromination while the N, N'-dibromodimethylhydantoin gave 55 per cent allylic bromination. The N-bromosuccinimide caused a smaller amount of tarry residue to be obtained in isolating the products from the reaction mixture than did N, N'-dibromodimethylhydantoin. When chloro- was used as a reaction solvent no allylic brominated product, 3-bromocyclohexene, could be isolated from the reaction mixture of either of the brominating agents. Only polybrominated materials were isolated. This is a good example of the role a solvent plays in certain reactions. In the less polar carbon tetrachloride solvent allylic bromination occurred presumably by a free radical type of mechanism. Polybrominated materials were also isolated which are assumed to have formed through an ionic type of mechanism.

Of the two brominating agents the N, N'-dibromodimethylhydantoin reacted more vigorously under the conditions used in the experiment, namely the reflux temperature of the reaction solvent, carbon

tetrachloride or chloroform. It also contains the higher percentage of active bromine, 55.5 per cent, as compared to 44.7 per cent for the N-bromosuccinimide.

In a search for a new and novel brominating agent two inorganic bromine containing compounds were prepared, nitrogen sulfide tetrabromide, $N_4S_4Br_4$, and phosphonitrilicbromide, $(PNBr_2)_{3 \text{ or } 4}$. The nitrogen sulfide tetrabromide was prepared in a 20 per cent yield, from the reaction of sulfur monochloride with ammonia followed by bromination of the initial reaction product. This compound was allowed to react several times with cyclohexene in carbon tetrachloride. However, mainly polybrominated cyclohexene could be isolated and only a small amount, 12.5 per cent of allylic bromination occurred. The phosphonitrilicbromide prepared from phosphorous pentabromide and ammonium bromide was allowed to react with cyclohexene in and in the absence of carbon tetrachloride as a solvent. During the attempted isolation of the products from this reaction mixture a strong decomposition occurred. No organic bromine products could be isolated and a study of the reactions between this reagent and cyclohexene was discontinued.

As was mentioned previously, the major part of the work reported here was devoted to an investigation of the mechanism of the Wohl Ziegler reaction. It has been known for over a decade, since the work of Buu-Hoi (1), that the typical N-bromoamides and imides not only are capable of allylic bromination but can also serve as nuclear brominating agents. The work of Schmidt and Karrer (54) demonstrated the effect of peroxides on the reaction. The use of peroxides in the reaction between N-bromosuccinimide and toluene resulted in side chain bromination. Peroxides also bring about the allylic bromination of olefins such as cyclohexene (60). It has been fairly well established that reactions induced by peroxide, ultra violet light and high temperature proceed through a free radical mechanism. It was demonstrated by Park (67) that the presence of Lewis type acids in the reaction between N-bromosuccinimide and toluene caused ring bromination to occur rather readily. The presence of occluded salts in the brominating agent has recently been shown (57) to cause ring bromination. Lewis acids are ionic type catalysts and as such promote an ionic mechanism.

The fact that N-bromoamides and imides can attack the allylic position of olefins and the side chain of toluene, the positions generally believed to react through a free radical mechanism suggests strongly such a mechanism for the Wohl Ziegler reaction (60). However, since the addition of bromine across an olefinic double bond (49,62) and nuclear substitution (67) with N-bromoamides have been observed it is very probable that an ionic mechanism is also operative in this reaction. Thus a plural mechanism is perhaps a better description of the processes involved in this reaction since it is likely that the N-bromoamides and imides may react by several mechanisms, resulting from homolytic as well as heterolytic dissociation of the reagent.

Any correct mechanistic concept will account for all the products obtained from the reaction. Thus, the true mechanism of the Wohl Ziegler reaction must account for allylic bromination of olefins, addition of bromine across a double bond, allylic shifts and introduction of the amide or imide nucleus onto an olefinic carbon and substitution of bromine into the aromatic nucleus. Further, the apparently considerable differences in reactivity of such brominating agents as N-bromosuccinimide, N-bromoglutarimide, N-bromophthalimide and N-bromohexahydrophthalimide in the allylic type of reaction should be accounted for in the mechanistic scheme.

Thus, the study of the infrared absorption spectra of some typical Wohl Ziegler allylic brominating agents, with particular reference to the carbonyl group, was undertaken. It was expected that any electrical effects influencing the nature of the nitrogen bromine bond due to variations in the structure of the brominating agent or its parent amide or imide would be transmitted through the carbonyl group of such compounds. It was hoped to correlate the absolute integrated absorption intensities, or the frequency, or the molar extension coefficient of the carbonyl band with the manner in which the N-bromoamides or imides function as brominating agents.

The photochemical and thermal decomposition was expected to give some measure of the relative tendencies of the N-bromoamides or imides towards homolytic dissociation of the nitrogen to bromine bond. Such ultra violet light induced decompositions are known to proceed through a free radical mechanism.

The third phase of the investigation into the mechanism of the Wohl Ziegler reaction involved the dark bromination of toluene at different temperatures. It was hoped to be able to correlate the amount of side chain bromination with the results of both the photochemical decomposition and the investigation of the infrared spectrum of the N-bromoamides and imides.

The investigation of the infrared absorption spectra of the N-bromoamides and their parent amides constitutes Part I of this thesis. However, any possible correlation between those studies and the results of the bromination of toluene has been retained for this part of the thesis. It was found for the N-bromoamides and also their parent amides that a linear relationship existed between the frequency of the carbonyl band and the absolute integrated absorption intensity. Further, it was found that a linear relationship existed between the effective electronegativity of the R group in the two molecules $R\text{-}\overset{O}{\overset{/\!/}{C}}\text{-}NH_2$ and $R\overset{O}{\overset{/\!/}{C}}\text{-}NHBr$, and both the carbonyl frequencies and the absolute integrated absorption intensities of the amide and N-bromoamide. It was expected that any electrical affects influencing the nature of the nitrogen bromine bond due to variations in the structure of either amides or imides would be transmitted through the carbonyl group of such compounds. Thus, as the carbonyl frequency of the amide or N-bromoamide shifted toward shorter wave lengths, and the absolute integrated absorption intensity decreased, and the effective electronegativity of the R group in the $R\overset{O}{\overset{/\!/}{C}}\text{-}NHBr$ structure increased, due to variations in the structure of the N-bromoamide, the tendency of

the nitrogen bromine bond to undergo heterolytic cleavage should increase. Thus, in the series $CCl_3C^{//O}$-NHBr, $CHCl_2C^{//O}$-NHBr and $CH_2ClC^{//O}$-NHBr the effective electronegativity of the R group decreases in the order

$$CCl_3- > CHCl_2- > CH_2Cl-$$

and both the wave length of the carbonyl frequency and the absolute integrated absorption intensity values decrease in the reverse order

$$CH_2Cl- > CHCl_2- > CCl_3- \quad .$$

If these measurements can be taken as a true measure of the relative tendency for heterolytic dissociation of the nitrogen to bromine bond then it would be expected that the N-bromotrichloroacetamide would give the greatest amount of ring bromination with toluene and N-bromomonochloroacetamide the least. The results of the bromination of toluene in the dark at 40°C. and 80°C. demonstrated that this was a very reasonable interpretation. At both temperatures the above order was observed. The results are listed in Table V.

TABLE V[a]

AMOUNT OF SIDE CHAIN AND RING BROMINATION OF TOLUENE WITH THE N-BROMOAMIDES AT 40° AND 80°C.

Brominating Agent	Percent Ring Bromination 40°C	80°C
$CCl_3C^{//O}$-NHBr	85.2	52.5
$CHCl_2C^{//O}$-NHBr	75.0	50.3
$CH_2ClC^{//O}$-NHBr	51.7	8.9

[a] Exactly 50 ml. of toluene and 0.05 mole of N-bromoamide used.

The molar extinction coefficients of the carbonyl band of N-bromo mono, di, and trichloroacetamide determined in carbon tetrachloride increase with increasing effective electronegativity of the R group, with decreasing wave length and with decreasing absolute integrated absorption intensity. Thus, if the molar extinction coefficient of the carbonyl band can be taken as a measure of the tendency of the nitrogen bromine bond to undergo heterolytic dissociation it would be expected that the N-bromoamide or imide having the higher molar extinction coefficient would give the greater amount of heterolytic dissociation. Conversely the lower the molar extinction coefficient the greater the tendency for homolytic cleavage of the nitrogen bromine bond.

The parent amides were included in the infrared investigation in order that the quality of the N-bromoamide, as a brominating agent, could be deduced from the spectral properties of the amide. That is, if the same trend in any one of several properties such as carbonyl frequency, absolute integrated absorption intensity, electronegativity of the substituent or molar extinction coefficient existed for the amide and the N-bromoamide it would be easier to measure such properties in the amide than in its N-bromo derivative as the latter are more difficult to obtain and purify. This relationship would of course depend on the legitimacy of these measurements as a means of predicting the quality of the N-bromoamide as a brominating agent. The same trend in the above measurements was found for the amides corresponding to their N-bromoamides. The carbonyl frequency for the parent amide and its N-bromo derivative was essentially the same and the absolute integrated absorption intensities were much lower for the N-bromoamides than for the parent amides.

The literature has a great deal of information concerning the photochemical decomposition of a wide variety of substances such as acetaldehyde, (78) chlorine dioxide (79) and hydrogen peroxide (80). However, no reference could be found in which the photochemical or thermal decomposition of the N-bromoamides and imides had been studied.

Reactions which are catalyzed by ultraviolet light such as the reaction between toluene and chlorine (34) to give benzyl chloride, benzal chloride and benzotrichloride are generally believed to proceed by a free radical type of mechanism. It was hoped that the photochemical and/or thermal decomposition studies of the N-bromoamides would give the relative rates of decomposition of the N-bromoamides from which their relative tendency for homolytic dissociation of the nitrogen bromine bond could be predicted. The results of the photochemical and thermal decomposition were not reproducable under the experimental conditions used, and the relative rates of decomposition of the N-bromoamides could not be determined from the rate of formation of bromine. The decompositions were all very slow with the mercury light source used and no decomposition occurred with a tungsten lamp. The ground glass beckman cells failed to prevent losses by evaporation of both the bromine produced in the decomposition and the carbon tetrachloride solvent. The theoretical amount of bromine which could be produced in such decompositions was never found, and on continued

radiation for long periods the bromine absorption decreased showing that some loss of the latter was occurring. Undoubtedly oxygen and surface catalysis very probably play a function in the decomposition causing some of the irregularity in the observed results. A light source of much greater intensity, such as a high pressure mercury arc, is necessary to facilitate the decomposition of the N-bromoamides. A more refined experimental system to prevent losses of bromine from the samples and the elimination or equalizing of oxygen and surface effects is required. However, it can be stated in a qualitative manner that N-bromomonochloroacetamide undergoes homolytic fission of the nitrogen bromine bond at the greatest rate to produce bromine, and N-bromotrichloroacetamide is the slowest to undergo such rupture of the nitrogen bromine bond. This statement is based on the observation that a solution of N-bromomonochloroacetamide was the first to develop the bromine color when solutions of the N-bromo, mono, di and trichloroacetamides of comparable concentration in carbon tetrachloride were set aside in ordinary room light. The N-bromotrichloroacetamide was the last to develop the color characteristic of bromine. This would indicate that, as expected, the smaller the electronegativity of the R group of the $RC\overset{O}{\nearrow}-NHBr$ the greater the tendency for homolytic fission of the nitrogen bromine bond. This is in good agreement with the infrared data in which the relative tendencies for homolytic and heterolytic rupture were investigated. Thus, it appears, based on these observations and conclusions, that only an inductive affect

is operating in controlling the manner in which the nitrogen to bromine bond ruptures in the reaction of the N-bromoamides with toluene.

Although no quantitative data was obtained from the photochemical and thermal decomposition studies of the N-bromoamides several significant observations were made. A study of the curve, Figure XVI, for the decomposition of N-bromotrichloroacetamide shows that initially the rate is slow, then increases to a steady rate, and then tapers off. This type of curve is characteristic of an autocatalytic type of reaction in which the products of the reaction catalyze the initial reaction. This autocatalysis is demonstrated more conclusively by Figure XVII which is a plot of the 415 millimicron band of bromine against time for the decomposition of solutions of N-bromotrichloroacetamide in carbon tetrachloride and N-bromotrichloroacetamide plus free bromine in carbon tetrachloride. Both solutions contained the same concentration in gram atoms of bromine. Figure XVII shows, by the increased slope of the curve representing the decomposition of the solution of the N-bromoamide and bromine, that the presence of bromine enhances the rate of decomposition of the N-bromoamide.

The second observation concerns the absorption peak of bromine in carbon tetrachloride. This peak was reported (77) to be at 415 millimicrons which was confirmed in the present studies during the preparation of the Beer's law curves, Figure XVIII. However, such was not the case for the bromine peak arising from both the photochemical

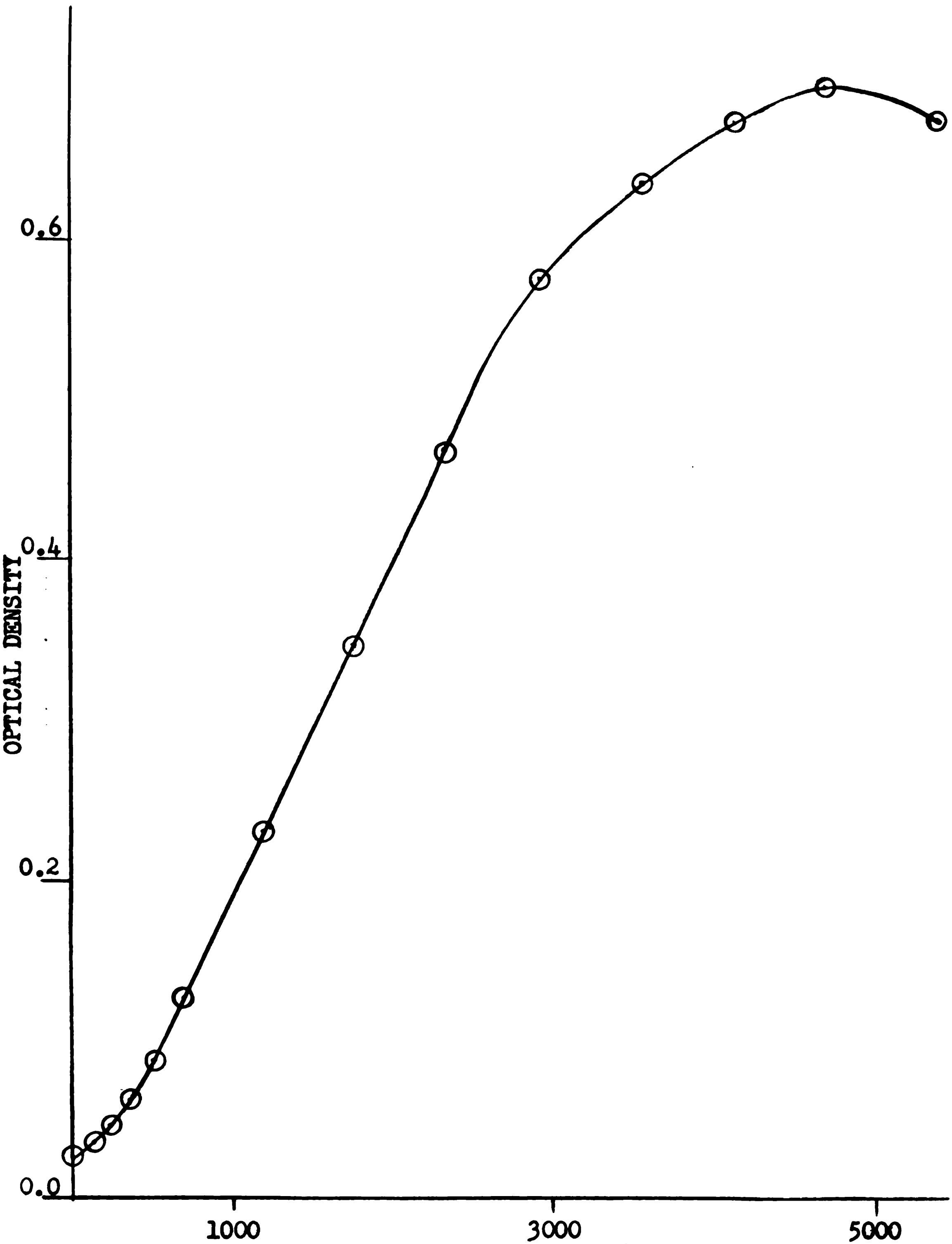


FIGURE XVI. OPTICAL DENSITY OF THE BROMINE ABSORPTION BAND VERSUS TIME OF IRRADIATION OF N-BROMOTRICHLOROACETAMIDE

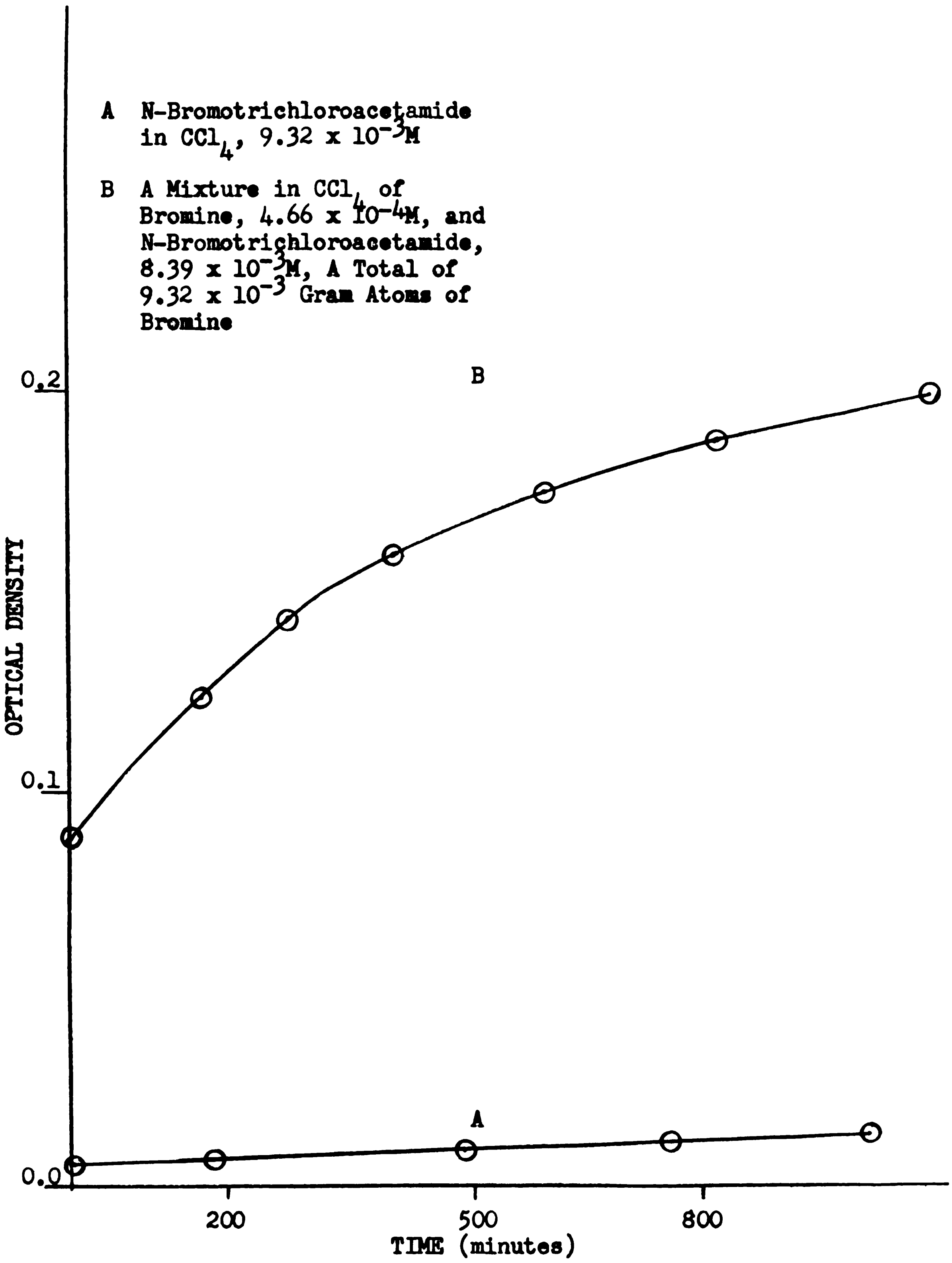


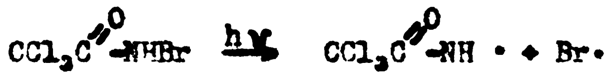
FIGURE XVII. OPTICAL DENSITY OF THE BROMINE ABSORPTION BAND VERSUS TIME OF N-BROMOTRICHLOROACETAMIDE DECOMPOSITION WITH AND WITHOUT ADDED BROMINE and thermal decomposition of the N-bromoamides. In the decomposition of the N-bromo mono, di, and trichloroacetamides the initial peak to appear was at 380 millimicrons. This peak gradually shifted to longer wave lengths as the decomposition proceeded until it reached a value of 408-410 millimicrons. At this wave length the peak reached its maximum intensity and did not shift further on prolonged irradiation or heating.

In the decomposition of the same N-bromoamides in the presence of bromine the peak, before irradiation with ultraviolet light or before heating, was at 415 millimicrons. As the decomposition proceeded the peak increased in intensity and shifted to shorter wave lengths until it reached a value of 408-410 millimicrons. From this point on no further shift was observed on continued irradiation or heating. The above data suggests that the bromine is complexed in some manner in the carbon tetrachloride solution of the N-bromoamide. Molecular complexes of the halogens with unsaturated hydrocarbons, alcohols and ethers have been known for some time (81,82,83,84). Iodine in particular has been reported (84) to form a one to one molecular complex with ethyl alcohol in benzene. Cryoscopic measurements supported such a conclusion.

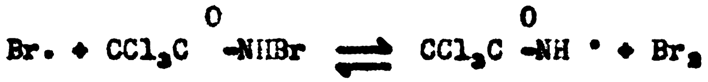
Thus, the assumption that bromine is complexed with something in the carbon tetrachloride solution of the N-bromoamide seems very reasonable. The question naturally arises as to the nature of the bromine complex and the extent to which it is complexed. From the above observations it can be concluded that the bromine is complexed with something which is formed as a result of the photochemical or thermal decomposition of the N-bromoamide. That is, the bromine peak of a solution of the N-bromoamide and bromine in carbon tetrachloride before decomposition coincided with the 415 millimicron peak of a solution of bromine in carbon tetrachloride. However, during the decomposition this peak shifted to shorter wave lengths, as low as 408-410 millimicrons. This shift could be caused either by the complexing of the bromine with something being formed as a result of the decomposition of the N-bromoamide or by the appearance of a new peak close to the 415 millimicron band for bromine leading to a shift of the bromine peak toward the new peak with a single combined resultant peak. In the decomposition of the N-bromoamides the first peak to appear was at 380 millimicrons. The solution at this time had the brown color characteristic of a dilute solution of bromine in carbon tetrachloride. There was no other peak present between 360 and 540 millimicrons. This peak was attributed to the bromine tied up in some manner with another product of the decomposition. The fact that the peak shifted toward longer wave lengths until it reached a maximum of 408 to 410 millimicrons indicated that the final and intermediate peak wave lengths could be attributed to a combination of the two peaks attributed to complexed and non-complexed bromine. That is, the first bromine resulting from the decomposition was completely complexed but as the decomposition proceeded non-complexed or free bromine was produced.

The nature of the complex is unknown. However, since the bromine is complexed with another product of the decomposition some reasonable speculation as to the nature of the complex can be offered. The thermally or ultraviolet light induced decomposition of N-bromotrichloroacetamide is the simplest case since in this case there is no possibility of any bromination reaction occurring.

The initial thermal or ultraviolet light induced dissociation can be expressed as



$$CCl_3\overset{O}{C}{-}NHBr \xrightarrow{h\nu} CCl_3\overset{O}{C}{-}NH\cdot + Br\cdot$$



$$Br\cdot + CCl_3\overset{O}{C}{-}NHBr \rightleftharpoons CCl_3\overset{O}{C}{-}NH\cdot + Br_2$$

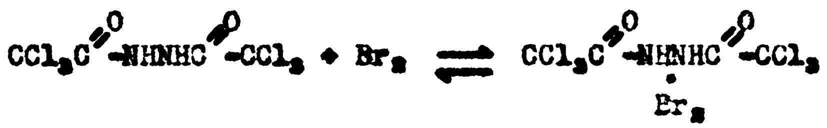
This latter step was shown by the increased rate of decomposition in the presence of bromine. A bromine sensitised reaction is one in which the initial step would be

$$Br_2 \xrightarrow{h\nu} 2Br\cdot$$

A chain termination step could follow

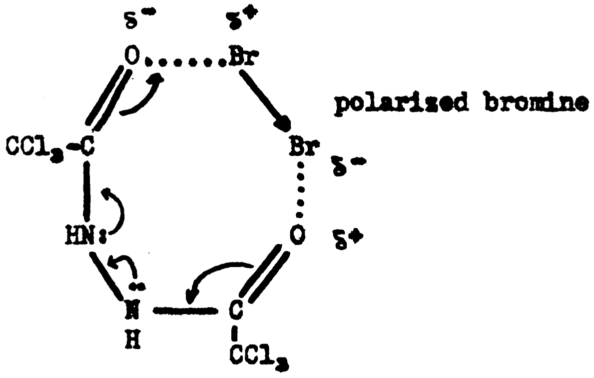
$$2\ CCl_3\overset{O}{C}{-}NH\cdot \longrightarrow CCl_3\overset{O}{C}{-}NHNH\overset{O}{C}{-}CCl_3 \ .$$

It is with this latter type of compound that the bromine could be complexed.



$$CCl_3\overset{O}{C}{-}NHNH\overset{O}{C}{-}CCl_3 + Br_2 \rightleftharpoons CCl_3\overset{O}{C}{-}NH\underset{\overset{\cdot}{Br_2}}{N}H\overset{O}{C}{-}CCl_3$$

One possible structure of this complex may be



The fact that the bromine peak does shift casts some doubt as to the validity of following the rate of decomposition of N-bromoamides by bromine absorption at 415 millimicrons.

The experimental evidence for the above speculation as to the relative tendency of the N-bromoamides to undergo heterolytic or homolytic fission of the nitrogen bromine bond naturally was based on the actual bromination reaction in which the individual N-bromoamides were employed as the brominating agent. The reactions were arranged so that they were carried out under identical conditions. Toluene was chosen as the compound to be studied in the bromination with the N-bromoamides since the products of the reaction show both allylic and nuclear attack, and in addition are easily isolated and analyzed. The amount of side chain bromination was taken to be a measure of the amount of homolytic fission of the nitrogen bromine bond. The difference between the amount of side chain bromination and the total bromination was the amount of ring bromination which was a measure of the amount of heterolytic fission of the nitrogen bromine bond.

TABLE VI[a]

RESULTS OF THE BROMINATION OF TOLUENE WITH BROMINE AND THE N-BROMOAMIDES AT 80°C.[b]

Brominating Agent		$CCl_3\overset{O}{C}-NHBr$	$CHCl_2\overset{O}{C}-NHBr$	$CH_2Cl\overset{O}{C}-NHBr$	Br_2
Amount	(grams or ml.	12.07 g.	10.34 g.	8.621 g.	1.25 ml.
	(moles	0.05	0.05	0.05	0.0244
	(milliequivalents[c]	50.0	50.0	50.0	24.38
Time for Completion of Reaction in Hours		2.5	6.0	12.0	4.5
Milliequivalents of Halogen	Distillate (active)	21.75	22.22	35.89	21.81
	(total)	45.63	44.89	39.39	23.25
	Residue total	7.54	8.22	10.16	0.61
Milliequivalents of Halogen in Residue due to Amide		3.64	3.60	0.00	——
Per Cent Conversion to Monobrominated Toluene		91.3	89.8	78.8	95.6
Per Cent Side Chain Bromination		47.5	49.7	91.1	93.7
Material Balance Per Cent		99.1	99.0	99.1	98.2

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[a] No amide was found in the distillates.

[b] Fifty ml. of toluene used in all experiments.

[c] Milliequivalents as a brominating agent.

TABLE VII

RESULTS OF THE BROMINATION OF TOLUENE WITH BROMINE AND THE N-BROMOAMIDES AT 40°C.

Brominating Agent		$\mathrm{CCl_3\overset{O}{\overset{\|}{C}}-NHBr}$[a]	$\mathrm{CHCl_2\overset{O}{\overset{\|}{C}}-NHBr}$	$\mathrm{CH_2Cl\overset{O}{\overset{\|}{C}}-NHBr}$	$\mathrm{Br_2}$
Amount	grams or ml.	12.07 g.	10.34 g.	8.621 g.	1.25 ml.
	moles	0.05	0.05	0.05	0.0244
	milliequivalents	50.0	50.0	50.0	24.38
Reaction Time in Hours		24.0	24.0	24.0	10.5
Milliequivalents of Unreacted Brominating Agent		0.24	18.31	42.03	0.00
Milliequivalents of Free Bromine		2.59	2.73	0.79	0.00
Milliequivalents of Halogen	Distillate (active)	5.05	4.28	2.54	20.69
	Distillate (total)	34.17	17.12	5.27	23.26
	Residue total	9.95	5.03	1.71	0.72
Per Cent Completeness of Reaction		99.5	63.4	15.9	100.0
Per Cent Conversion to Monobrominated Toluene		68.3	54.1	69.6	95.6
Per Cent Side Chain Bromination		14.8	25.0	48.3	89.0
Material Balance Per Cent		84.7	86.4	98.6	98.5

[a] In the reaction of N-bromotrichloroacetamide with toluene 4.62 of the 9.95 milliequivalents of halogen found in the residue was due to unseparated amide. No amide was found in the residue of the other reactions.

Tables VI and VII summarize the reactions of N-bromo mono, di, trichloroacetamides and bromine with toluene at two different temperatures, 40° and 80°C. Bromine was allowed to react with toluene to provide a standard with which the other brominating agents could be compared.

The reactions of the N-bromoamides with toluene at 80°C. were allowed to run to completion. The reaction went through a series of color changes from clear to yellow, to brown, to red, and back to yellow again. There was no evolution of hydrogen bromide detected during these reactions. The N-bromomonochloroacetamide showed the largest amount, 91.1 per cent, of free radical side chain bromination and the smallest amount, 8.9 per cent, of ionic or ring bromination. The N-bromotrichloroacetamide showed the smallest amount, 47.5 per cent side chain bromination and the largest amount 52.5 per cent, of ring bromination. These were the results anticipated from the infrared and decomposition data. The integrated absolute intensity values, electronegativity values, and carbonyl frequencies indicated that N-bromotrichloroacetamide should be the most likely of the N-bromoamides to undergo heterolytic fission of the nitrogen bromine bond and that N-bromomonochloroacetamide the least likely to undergo heterolytic fission of the same bond. The experimental results of the bromination of toluene were in good agreement with this prediction.

The N-bromotrichloroacetamide showed the highest conversion, 91.3 per cent, to monobrominated product and the smallest amount, 8.7 per cent, of polybrominated product. The N-bromomonochloroacetamide, which gave the greatest amount of side chain bromination, showed the smallest, 78.8 per cent, conversion to monobrominated product and the largest amount, 21.2 per cent, of polybrominated product. Thus, the greater the side chain bromination the more polybrominated product.

The material balance for the reactions carried out at 80°C. was at least 99 per cent in all cases studied.

The reactions of the N-bromoamides with toluene carried out at 40°C. were allowed to proceed for exactly twenty-four hours, in which time none of the reactions were complete. The same general results were found in the reactions of the N-bromoamides with toluene at 40°C. as had been observed at 80°C. That is, the same order was observed in the ratio of side chain and ring bromination of toluene. The N-bromomonochloroacetamide gave the highest amount of side chain bromination and the smallest amount of ring bromination. The N-bromotrichloroacetamide gave the smallest amount of side chain bromination and the largest amount of ring bromination. The amount of side chain bromination was much less for the reactions at 40°C. than for those at 80°C. These results were also in agreement with those predicted from the infrared and decomposition studies of the brominating agents. The relative rates of reaction were also the same at 40°C. and at 80°C. That is, the reaction of the N-bromotrichloroacetamide with toluene at 80°C. was completed in 2.5 hours; whereas, the N-bromomonochloroacetamide reaction was the slowest of those studied and was complete only after a twelve hour period. At 40°C. the N-bromotrichloroacetamide reaction was 99.5 per cent complete after 24 hours and the N-bromomonochloroacetamide reaction was the least complete, 15.9 per cent, in the same period of time.

The most interesting observation made from the reactions carried out at 40°C. was the fact that molecular bromine was isolated in each of the reactions of the N-bromoamides with toluene. In the case of the N-bromotrichloroacetamide 5.2 per cent of the bromine from the reacted N-bromoamide was isolated in the form of free bromine. In the case of the N-bromodichloroacetamide 8.6 per cent was obtained in the form of free bromine, and in the case of the N-bromomonochloroacetamide 9.9 per cent was determined in the form of free bromine. Thus, the general trend was that the reaction which showed the formation of the greater per cent of free bromine gave the larger per cent of side chain bromination.

In two reactions at 40°C. the material balance was a little low, 85 per cent. This was due to the decomposition of the unreacted N-bromoamide after it had been isolated and before it was analyzed. The free bromine formed caused low results in the iodimetric determination of the unreacted N-bromoamide. By reducing the bromine with sulfur dioxide and redetermining the N-bromoamide a correction could be applied so that a material balance of 95 per cent was obtained.

The reaction of molecular bromine with toluene at 40°C. and at 80°C. gave 89 and 94 per cent, respectively, of side chain bromination. This was a higher yield of side chain bromination than any of the N-bromoamides. Bromine also gave a higher percentage of monobrominated product, 95.6 per cent, than any of the N-bromoamides at both 40°C. and 80°C. The reaction time for bromine with toluene at 40°C. was shorter than for any of the N-bromoamides. At 80°C. the N-bromotrichloroacetamide reacted at a faster rate than molecular bromine.

The fact that there was bromine present, after a period of twenty-four hours, in the reaction mixture of N-bromotrichloroacetamide and toluene when essentially all of the N-bromoamide had reacted, coupled with the fact that the reaction of bromine with toluene was completed in less than half that time strongly suggested that the bromine found in the reaction of the N-bromoamide with toluene was complexed in some manner. It was shown in the decomposition studies of the N-bromoamides that bromine arising as a result of the decomposition of such compounds was complexed with an unknown product formed in the decomposition of the N-bromoamide but not with the latter itself. It is not known whether the bromine could be complexed with the amide which was the byproduct of the bromination of toluene by the N-bromoamides. This amide could not arise from the decomposition of the N-bromotrichloroacetamide in carbon tetrachloride solution.

Park, Gerjovich, Lycan and Lacher (67) carried out a study of the bromination of toluene with a series of N-bromoamides which included the N-bromo mono, di, and trichloroacetamides. The results of the bromination of toluene presented in the present work are in some disagreement with the data of Park and his co-workers (67). Tables VIII and IX summarize the obvious discrepancies.

TABLE VIII

RESULTS OBTAINED BY PARK ON THE BROMINATION OF TOLUENE WITH THE N-BROMOAMIDES (67)

Brominating Agent	Conversion to C_7H_7Br Per Cent	$BrC_6H_4CH_3$ Per Cent	$C_6H_5CH_2Br$ Per Cent
$CCl_3\overset{O}{C}-NHBr$	58	17	83
$CHCl_2\overset{O}{C}-NHBr$	64	62	38
$CH_2Cl\overset{O}{C}-NHBr$	70	82	18

TABLE IX

RESULTS OF THE BROMINATION OF TOLUENE WITH THE N-BROMOAMIDES AT 80°C. AND 40°C.

Brominating Agent	Temperature $^\circ$C.	Conversion to C_7H_7Br Per Cent	$BrC_6H_4CH_3$ Per Cent	$C_6H_5CH_2Br$ Per Cent
$CCl_3\overset{O}{C}-NHBr$	80.1	91.3	52.5	47.5
$CHCl_2\overset{O}{C}-NHBr$	80.0	89.8	50.5	49.5
$CH_2Cl\overset{O}{C}-NHBr$	80.0	78.8	8.9	91.1
$CCl_3\overset{O}{C}-NHBr$	40.0	68.6	85.2	14.8
$CHCl_2\overset{O}{C}-NHBr$	40.0	54.1	75.0	25.0
$CH_2Cl\overset{O}{C}-NHBr$	40.0	69.6	51.7	48.3

It can be seen from these tables that the disagreement lies in the ratio of side chain to ring bromination by the N-bromomono and trichloroacetamides. The work of Park and his co-workers indicated that the N-bromotrichloroacetamide gave the highest ratio of side chain to ring bromination, and that the N-bromomonochloroacetamide gave the lowest ratio of side chain to ring bromination. The results of the work presented in this thesis are just the opposite. The N-bromotrichloroacetamide gave the lowest ratio of side chain to ring bromination, while the N-bromomonochloroacetamide gave the highest ratio of side chain to ring bromination.

The experimental conditions were somewhat different. In this work the experiments were carried out in constant temperature baths at 40°C. and 80°C.; whereas, in Park's work the reactants were mixed presumably at room temperature and then heated at the reflux temperature of toluene to ensure completion of the reaction. It seems highly unlikely that this difference in conditions could account for the discrepancy between the results. It is difficult to offer a reasonable explanation for the differences between the two sets of data.

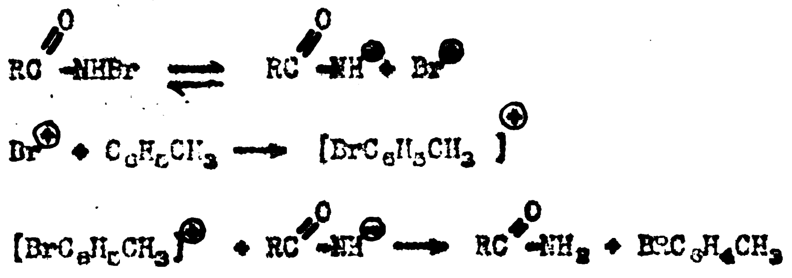
Park (67) related the absorption coefficient of the N-H fundamental band at 2.93 u to the brominating activity of the nitrogen bromine bond and found that the larger the absorption coefficient the greater the amount of ring bromination. The electronegativity of the "R" group of the $\mathrm{R\overset{\nearrow O}{C}-NHBr}$ structure did not agree with the bromination data.

The bromination data presented in this thesis and shown to be a measure of the brominating activity of the nitrogen bromine bond was correlated with the molar extinction coefficient of the carbonyl band of the N-bromoamides, the absolute integrated absorption intensity of the carbonyl band of the N-bromoamides and their parent amides, the wave length of the carbonyl band peak of the N-bromoamides and their parent amides, and with the effective electronegativity of the "R" group of the $\overset{O}{RC}-NHBr$ and $\overset{O}{RC}-NH_2$ structures.

It was found that the greater the molar extinction coefficient the lower the absolute integrated absorption intensity, the shorter the wave length of the carbonyl band and the higher the effective electronegativity of the "R" group, the greater the amount of ring bromination. The carbonyl group was chosen for these measurements because of its relatively high absorption intensity, and in particular because it was felt that any effects of structure contributing to the mechanism of the reaction would manifest themselves in the carbonyl group.

In agreement with the data from the bromination of toluene at 80°C. and at 40°C. the following mechanistic scheme appears reasonable.

Bromination by an Ionic Mechanism



$$\overset{O}{\overset{\|}{RC}}-NHBr \rightleftharpoons \overset{O}{\overset{\|}{RC}}-NH^{\ominus} + Br^{\oplus}$$

$$Br^{\oplus} + C_6H_5CH_3 \longrightarrow [BrC_6H_3CH_3]^{\oplus}$$

$$[BrC_6H_5CH_3]^{\oplus} + \overset{O}{\overset{\|}{RC}}-NH^{\ominus} \longrightarrow \overset{O}{\overset{\|}{RC}}-NH_2 + BrC_6H_4CH_3$$

Bromination by a Radical Mechanism

$R\overset{O}{\overset{/\!/}{C}}-NHBr \rightleftharpoons R\overset{O}{\overset{/\!/}{C}}-NH\cdot + Br\cdot$

With N-bromoamides

$R\overset{O}{\overset{/\!/}{C}}-NH\cdot + C_6H_5CH_3 \rightleftharpoons R\overset{O}{\overset{/\!/}{C}}-NH_2 + C_6H_5CH_2\cdot$

$C_6H_5CH_2\cdot + R\overset{O}{\overset{/\!/}{C}}-NHBr \longrightarrow C_6H_5CH_2Br + R\overset{O}{\overset{/\!/}{C}}-NH\cdot$

With Bromine

$Br\cdot + R\overset{O}{\overset{/\!/}{C}}-NHBr \rightleftharpoons R\overset{O}{\overset{/\!/}{C}}-NH\cdot + Br_2$ Bromine Sensitization

$Br_2 \rightleftharpoons 2Br\cdot$

$Br_2 + A \rightleftharpoons [A\ Br_2]$ Complex Formation

$Br\cdot + C_6H_5CH_3 \rightleftharpoons C_6H_5CH_2\cdot + H\ Br$

$Br_2 + C_6H_5CH_2\cdot \longrightarrow C_6H_5CH_2Br + Br\cdot$

$H\ Br + RC-NHBr \longrightarrow R\overset{O}{\overset{/\!/}{C}}-NH_2 + Br_2$

Bromination by the Complex

$[A\ Br_2] + C_6H_5CH_2\cdot \longrightarrow A + C_6H_5CH_2Br + Br\cdot$

$[A\ Br_2] \rightleftharpoons [A\ Br]^{\mp} + Br^{\oplus}$

$[A\ Br]^{\pm} + Br^{\pm} + C_6H_5CH_3 \longrightarrow A + BrC_6H_4CH_3 + H\ Br$

Chain Termination

$Br\cdot + C_6H_5CH_2\cdot \longrightarrow C_6H_5CH_2Br$

$2R\overset{O}{\overset{/\!/}{C}}-NH\cdot \longrightarrow R\overset{O}{\overset{/\!/}{C}}-NHNH\overset{O}{\overset{/\!/}{C}}-R$

The first three steps represent the ionic bromination of toluene by the N-bromoamides. The first and fourth steps in the mechanistic scheme represent the primary heterolytic and homolytic dissociation of the nitrogen bromine bond. The fourth step through the fifth to the last represent both the free radical bromination of toluene by bromine and N-bromoamides.

The infrared and decomposition data supported by the bromination data showed that as the electronegativity of the R group of the $R\overset{O}{C}-NHBr$ structure increased the first step, heterolytic dissociation, was favored over the fourth step, homolytic dissociation. Thus, the ionic bromination mechanism was supported by the results of the bromination of toluene in which the N-bromotrichloroacetamide gave the highest ratio of ring to side chain bromination and the N-bromomonochloroacetamide the smaller ratio of ring to side chain bromination. The results of the bromination of toluene showed that under the conditions of the reaction the products obtained were determined primarily by the relative tendency of the N-bromoamide to undergo heterolytic or homolytic dissociation as indicated by the first and fourth steps in the mechanistic scheme. The tendency to undergo heterolytic or homolytic fission was governed by the electronegativity of the substituents in the amide attached to the carbonyl carbon.

The increase in reaction temperature from 40°C. to 80°C. gave an increase in the amount of side chain bromination. The rate of free radical reactions is generally increased by an increase of temperature. The decrease in the ratio of ring to side chain bromination with increasing temperature demonstrated the dual nature of the mechanism. If only one mechanism were responsible for the bromination reaction the ratio of side chain to ring bromination would not change with a change in temperature.

Bromine reacted with toluene at 40°C. and at 80°C. predominately by a free radical mechanism. This was shown by the high ratio of side chain to ring bromination and the small change in the ratio of side chain to ring bromination between the two temperatures.

The rate determining step in the ionic bromination would appear to be the initial heterolytic dissociation of the nitrogen bromine bond. The rate determining step in the radical bromination would appear to be the initial homolytic dissociation of the nitrogen bromine bond. However, the role of the bromine complex is not yet certain, especially since such a relatively large amount of molecular bromine was found in the reaction mixture. It is not known whether the bromine complex leads to ring or side chain bromination. It is not known whether the bromine complex is a separate part of the mechanism or whether it is an intrinsic part of the ionic and radical mechanisms. The bromine is loosely bound in the complex since it can be readily removed by vacuum distillation.

The reaction of hydrogen bromide with the N-bromoamide was included in the mechanism because of the possibility of the reaction of free or complexed bromine, formed during the reaction of the N-bromoamide with toluene, giving hydrogen bromide. The excellent material balance obtained in the reactions at 80°C. preclude any loss of bromine in the form of hydrogen bromide.

A kinetic investigation would greatly help in an understanding of the radical mechanism.

The results of this work are not complete enough to allow for any sweeping generalisations. It would be expected from the infrared data that the N-bromoacetamide would give the greatest amount of side chain bromination and that N-bromotrifluoroacetamide would give the smallest amount of side chain bromination. The reported (67) reactions of these two reagents with toluene tend to support this prediction.

The correlation between the infrared data and the method of dissociation of the nitrogen bromine bond seems to hold for the N-bromoamides. However, it is not known if this same technique could be utilised with the N-bromoimides. Substances like N-bromosuccinimide and N,N'-dibromodimethylhydantoin are good radical brominating agents; hwereas, N-bromoglutarimide and N-bromohexahydrophthalimide are not as good. Quite possibly the bromine complex plays a major role in the reaction and should be thoroughly investigated.

EXPERIMENTAL

EXPERIMENTAL

Reagents and Apparatus

The chloroform solvent was washed with concentrated sulfuric acid at 50°C. then with distilled water, followed by drying over calcium chloride, after which it was distilled.

Carbon tetrachloride was washed successively with 10 per cent potassium hydroxide solution, concentrated sulfuric acid and distilled water. It was then dried over calcium chloride and distilled.

Cyclohexene was allowed to stand continuously in contact with an aqueous ferrous sulfate solution and distilled as needed.

Trifluoroacetic acid was distilled from 25 g. of phosphorous pentoxide using a 30 cm. by 2 cm. bore column packed with glass helices.

Toluene was dried over calcium chloride and distilled as needed.

The N-bromoamides and imides were recrystallised from carbon tetrachloride and their purity determined iodimetrically.

The melting points were determined using capillary tubes in a silicone oil bath and were uncorrected.

Preparation of Phosphonitrilic Bromide, $PNBr_2$ (68)

Into a two liter three neck round bottom flask was placed 541.5 g., 2.0 moles, of phosphorous tribromide. At room temperature, 320 g., 2.0 moles, of liquid bromine was added slowly over a period of four hours. A yellow solid, phosphorous pentabromide formed. Then one liter of symmetrical tetrachloroethane was added followed by 245 g., 2.5 moles, of ammonium bromide. The reaction mixture was then heated at its reflux temperature for twenty-four hours at which point no further evolution of hydrogen bromide took place. Small amounts of bromine were added periodically to replace that lost due to dissociation of the phosphorous pentabromide. The solvent was then removed by distillation leaving a crystalline slurry which on recrystallization from benzene gave a white crystalline solid. This phosphonitrilic bromide is reported (69) to be a mixture of the trimer and the tetramer. However, for the purposes of this investigation the separation of the isomers was deemed unnecessary. The weight of pure phosphonitrilic bromide was 164 g., 0.8 moles, a yield of 40 per cent based on the amount of phosphorous tribromide used. The material melted at 192-193°C. The reported melting point (69) for the trimer is 191°C. and for the tetramer 201°C. (69).

The reactions involved are represented by the following equations:

$$PBr_3 + Br_2 \longrightarrow PBr_5$$

$$PBr_5 + NH_4Br \longrightarrow PNBr_2 + 4\ HBr$$

Preparation of Nitrogen Sulfide, N_4S_4 (70)

Into a one liter three neck flask fitted with a stirrer, gas inlet and reflux condenser were placed 20 ml., 33.7 g., 0.25 moles, of sulfur monochloride and 600 ml., 5.75 moles, of anhydrous ethyl ether.

Ammonia gas was then bubbled into the above cooled, stirred, reaction solution at a rate of 900 to 1000 ml. per minute. The reaction, as it proceeded, went through a color change from yellow to brown and finally to orange at the completion of the reaction. The reaction was completed in two hours, after which the reaction mixture was set aside overnight. An orange solid separated from the solution which itself was a bright red color. The solid was separated by filtration and then extracted with several portions of anhydrous ethyl ether. The other extract was allowed to evaporate at room temperature leaving a solid residue of orange crystals with a characteristic odor. The pure nitrogen sulfide weighed 1.5 g., 0.008 moles, which is a 20 per cent yield based on the amount of sulfur monochloride used. The material melted at 177-178°C. Its reported (70) melting point is 178°C.

The reactions involved are represented by the following equation:

$$16\ NH_3 + 6\ S_2Cl_2 \longrightarrow 12\ NH_4Cl + N_4S_4 + 8\ S$$

This preparation was repeated several times to obtain enough starting material for the synthesis of nitrogen sulfide bromide.

Preparation of a Nitrogen Sulfide Bromide, $N_4S_4Br_4$ (71)

Into a one liter three neck flask fitted with a stirrer, reflux condenser and a dropping funnel were placed 16.35 g., 0.09 moles, of nitrogen sulfide and 500 ml., 5.2 moles, of reagent grade carbon tetrachloride. To the stirred mixture, kept at 40°C., 32.0 g.,

0.2 moles, of liquid bromine was added dropwise over a period of two hours. The reaction mixture was stirred for an additional eleven hours at 40°C. and then filtered to remove any unreacted nitrogen sulfide. The filtrate was evaporated by means of an aspirator and on careful heating to remove the last traces of solvent yielded a bronze colored amorphous solid. No physical constants could be found in the literature for the nitrogen sulfide bromides. However, the bronze color corresponds to that which has been reported (72) for nitrogen sulfide tetrabromide. The bronze solid obtained by the above procedure liberated bromine at temperatures above 150°C. to give a white amorphous solid which did not melt at temperatures up to 250°C. The weight of the above material was 28.2 g., 0.056 moles, which is a yield of 62 per cent based on the amount of nitrogen sulfide used and the assumption that the compound formed is the nitrogen sulfide tetrabromide.

The Reaction of Phosphonitrilic Bromide with Cyclohexene

Into a half liter, two neck flask fitted with a stirrer and a reflux condenser were placed 20.5 g., 0.1 mole, of phosphonitrilic bromide and 75 ml., 0.78 mole, of reagent grade carbon tetrachloride. To this stirred mixture, heated on a steam bath, was added 50 ml., 0.49 mole, of cyclohexene which had just been washed with aqueous ferrous sulfate and freshly distilled. The stirred reaction mixture was heated at its reflux temperature on the steam bath for three hours, during which time there was no evidence of hydrogen bromide being formed. The carbon tetrachloride and excess cyclohexene were removed by distillation at atmospheric pressure leaving a white crystalline solid. The solid was dried under vacuum, and on being set aside overnight it turned almost black. On recrystallization from carbon tetrachloride the black solid gave two solids, one of which was pure phosphonitrilic bromide which had a melting point of 194-195°C. Its reported (69) melting point is 191°C. for the trimer and 201°C. for the tetramer. The second black solid was of unknown composition and did not melt at temperatures up to 230°C.

The reaction between phosphonitrilic bromide and cyclohexene was repeated. In the same apparatus as described above were placed 9.2 g., 0.045 mole, of phosphonitrilic bromide and 68 ml., 0.67 mole, of cyclohexene which had been freshly purified by washing with aqueous ferrous sulfate and distilling. This reaction differed from the one previously described in that no carbon tetrachloride was used as a solvent. The heterogeneous mixture was stirred and heated on the steam bath for four hours, during which time not all of the phosphonitrilic bromide reacted. The reaction mixture was filtered and the solid washed with carbon tetrachloride. The carbon tetrachloride solution was combined with the original filtrate. The solid after being dried weighed 7.4 g., 0.036 mole, and represented 80 per cent of the starting material phosphonitrilic bromide as judged by a mixed melting point, 192-193°C., with an authentic sample of phosphonitrilic bromide. The combined filtrate and carbon tetrachloride solution was distilled at atmospheric pressure to remove the carbon tetrachloride and excess cyclohexene. When the boiling point reached 83°C. a violent decomposition took place. At the time of the decomposition there was approximately 30 ml. of a yellow liquid in the distilling flask. After the decomposition only a black non-combustible solid remained. No satisfactory explanation for this decomposition can be offered at the present time.

The Reaction of Nitrogen Sulfide Tetrabromide with Cyclohexene

Into a half liter, two neck flask fitted with a stirrer and reflux condenser were placed 45.5 g., 0.09 mole, of nitrogen sulfide tetrabromide and 75 ml., 0.78 mole, of reagent grade carbon tetrachloride. This mixture was stirred and then brought to its reflux temperature on a steam bath at which point 41.1 g., 0.5 mole, of cyclohexene, which had just previously been washed with aqueous ferrous sulfate and distilled, was added. The reaction mixture was heated at its reflux temperature for six hours and then allowed to cool to room temperature; whereupon, a dark brown solid separated from the reaction mixture. The solid was removed by filtration and washed with several portions of cold carbon tetrachloride and these were combined with the original filtrate. The solid, amounting to 9.5 g., did not melt at temperatures up to 250°C. and was not identified. The combined filtrate and carbon tetrachloride washings were distilled at atmospheric pressure to remove the carbon tetrachloride and excess cyclohexene. The residual liquid was fractionally distilled under vacuum. Two grams of a pale yellow liquid, b.p. 69-72°C./ 13 mm., and 10.0 g. of a yellow liquid, b.p. 99-101°C./13 mm., were obtained.

The first fraction gave a positive test with alcoholic silver nitrate solution, indicating an allylic bromine atom and gave a positive test with aqueous potassium permanganate solution which indicated an unsaturated compound. The refractive index of the compound was n_D^{20} 1.5235 which is comparable to the refractive index, n_D^{20} 1.5230, reported (73) for 3-bromocyclohexene. The second fraction turned black when exposed to moist air. This darkening property of the second fraction and its boiling point, 99-101°C./13 mm., are identical to the properties reported (74) for 1,2-dibromocyclohexene.

Reaction of N-Bromosuccinimide with Cyclohexene in Chloroform

Into a half liter, one neck flask fitted with a reflux condenser were placed 17.8 g., 0.1 mole, of N-bromosuccinimide, 125 ml., 1.55 moles, of chloroform and 41.1 g., 0.5 mole, of cyclohexene which had previously been washed with aqueous ferrous sulfate and distilled. The reaction mixture was maintained at its reflux temperature for four hours, in which time the reaction was complete as indicated by the absence of any color formation in the reaction mixture when tested with an aqueous starch and potassium iodide solution. On cooling the reaction mixture in an ice bath a solid precipitated from solution which was removed by filtration and dried under vacuum. This material weighed 5.0 g., 0.05 mole, and had a mixed melting point of 124-126°C.

when mixed with succinimide which is identical with the melting point of the latter when pure. The filtrate was distilled at atmospheric pressure to remove the excess chloroform and cyclohexene. Attempted fractional distillation of the residual liquid under vacuum resulted only in decomposition and no identifiable products were isolated. Apparently only high boiling materials were present. This reaction was repeated four times and in no case did any allylic bromination occur.

The Reaction of N-Bromosuccinimide with Cyclohexene in Carbon Tetrachloride

Into a half liter, two neck flask fitted with a stirrer and reflux condenser were placed 17.8 g., 0.1 mole, of N-bromosuccinimide, 41.1 g., 0.5 mole, of cyclohexene and 75 ml., 1.2 moles, of carbon tetrachloride. The reaction mixture was stirred and heated at its reflux temperature for an hour and a half, in which time the reaction was complete as indicated by the absence of a color formation with an aqueous starch and potassium iodide solution. The end of the reaction was further indicated by the presence of a solid floating on top of the reaction solution. The reaction mixture was cooled in an ice bath and then filtered to recover the white solid which after drying under vacuum melted at 125-126°C., the same as succinimide. The succinimide weighed 9.4 g., 0.095 mole, representing a 95 per cent recovery of this byproduct. The filtrate was distilled at atmospheric pressure to remove excess cyclohexene and carbon tetrachloride. The residual liquid was then distilled under vacuum to yield a yellow liquid with a boiling point of 69-72°C./13 mm. It gave a positive test with an alcoholic silver nitrate solution indicating an allylic bromine atom and also gave a positive test for unsaturation with a solution of bromine in carbon tetrachloride. Its refractive index was n_D^{20} 1.5233 which is quite comparable to the refractive index, n_D^{20} 1.5230 reported (73) for 3-bromocyclohexene. This product weighing 10.1 g., 0.63 mole, represented a 63 per cent yield of 3-bromocyclohexene based on the amount of N-bromosuccinimide used. A black tarry residue weighing 3.5 g. remained after the distillation.

The Reaction of N,N'-Dibromodimethylhydantoin with Cyclohexene in Chloroform

Into a half liter, one neck flask fitted with a reflux condenser were placed 150 ml., 1.65 moles, of chloroform and 41.1 g., 0.5 mole, of cyclohexene which had just previously been distilled after washing with aqueous ferrous sulfate. To this solution was added 28.6 g., 0.5 mole, of N,N'-dibromodimethylhydantoin. An exothermic reaction set in liberating sufficient heat to the reaction mixture to heat it to its reflux temperature in five minutes. At the end of twenty minutes the reaction mixture had stopped refluxing and a homogenous solution resulted, at which point the reaction was not complete as indicated by the development of a black color when a drop of the reaction solution was tested with a starch iodide solution. External heat was then applied to bring the reaction solution to its reflux temperature, at which temperature it was kept for an hour and a half to complete the reaction. The apparatus was immediately arranged

for distillation and some of the excess cyclohexene and chloroform were distilled at atmospheric pressure. The residual liquid was then cooled in an ice bath and a solid separated from solution which was recovered by filtration, and after drying under vacuum had a melting point of 172-174°C. The melting point of pure dimethylhydantoin is reported (75) to be 175°C. The solid weighed 8.6 g., 0.07 mole, which was a 68 per cent recovery of this byproduct. Attempted distillation of the filtrate under vacuum caused extensive decomposition resulting in a black viscous mass from which no identifiable material could be isolated.

The Reaction of N,N'-Dibromodimethylhydantoin with Cyclohexene in Carbon Tetrachloride

Into a half liter, two neck flask fitted with a stirrer and a reflux condenser were placed 14.3 g., 0.05 mole, of N,N'-dibromodimethylhydantoin and 75 ml., 1.2 moles, of carbon tetrachloride. To this stirred mixture was added 41.1 g., 0.5 mole, of cyclohexene which had been freshly distilled after first being washed with aqueous ferrous sulfate. The reaction mixture was heated at its reflux temperature for one hour, at which time it gave a negative test with aqueous starch and potassium iodide solution. The reaction mixture was allowed to cool to room temperature and the solid which separated from solution was recovered by filtration and after drying under vacuum had a melting point of 172-174°C. The reported (75) melting point for pure dimethylhydantoin is 175°C. The weight of this byproduct was 5.5 g., 0.04 mole, which was an 86 per cent recovery of the dimethylhydantoin. The filtrate was distilled at atmospheric pressure to remove the excess cyclohexene and carbon tetrachloride, and the residual liquid was then distilled under vacuum to yield a yellow liquid which had a b.p. 69-72°C./13 mm. This material gave a positive test for allylic bromine with an alcoholic silver nitrate solution and a positive test for unsaturation with aqueous potassium permanganate solution. It had a refractive index of n_D^{20} 1.5239. The refractive index reported (73) for pure 3-bromocyclohexene is n_D^{20} 1.5230. The weight of the 3-bromocyclohexene was 8.9 g., 0.06 mole, which corresponds to a yield of 55 per cent. A dark tarry residue weighing 5.0 g. remained in the distillation equipment.

Preparation of N-Bromomonochloroacetamide in the Dark[a] (67)

Into a one liter, two neck flask fitted with a condenser and stirrer were placed 200 ml. of anhydrous trifluoroacetic acid and 23.0 g., 0.1 mole, of silver oxide. This mixture was cooled slightly and stirred until all of the silver oxide had reacted. Then at room temperature 18.7 g., 0.2 mole, of monochloroacetamide was added in several portions, the last of which was rinsed into the flask with 50 ml. of anhydrous trifluoroacetic acid. This mixture was stirred for one hour. Then 32 g., 0.2 mole, of chilled bromine dissolved in

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[a] The reaction flask was covered with a bag made from lightproof black paper used to protect photographic papers. During distillations and other experimental manipulations the apparatus was similarly protected against light.

50 ml. of anhydrous trifluoroacetic acid were added dropwise over a two hour period. The reaction mixture was stirred for an additional hour after the addition of the bromine was complete. The reaction mixture was then filtered to remove the silver bromide which was washed with three 25 ml. portions of chilled, anhydrous trifluoroacetic acid. The filtrate and wash solutions were combined and distilled at room temperature and a pressure of 10 mm. The trifluoroacetic acid and excess bromine were collected in a large trap which was cooled in a dry ice and isopropyl alcohol bath. After all of the trifluoroacetic acid and bromine were removed a yellowish oil remained. The pressure was immediately decreased to 1 mm. for several hours until only a yellow crystalline solid was left. It was found in earlier preparations of N-bromomonochloroacetamide that if the yellowish oil was set aside at room temperature for several hours decomposition took place and the yield of product was small. Freezing of this yellow oil also failed to produce crystals.

The yellow solid residue was recrystallized twice from carbon tetrachloride in the dark to give 20.0 g., 0.12 mole, of pure N-bromomonochloroacetamide which had a melting point of 74-74.5°C. The melting point reported (67) for this compound is 75°C. The yield of the product was 58 per cent based on the amount of chloroacetamide used. The purity of the compound was determined by an iodimetric determination of the per cent of bromine in the compound. It was found that the solid had 46.36 per cent bromine. The calculated value is 46.37 per cent bromine.

Preparation of N-Bromodichloroacetamide in the Dark (67)

Into a one liter, two neck flask fitted with a condenser and stirrer were placed 200 ml. of anhydrous trifluoroacetic acid and 23.0 g., 0.1 mole, of silver oxide. This misture was heated gently and stirred until a homogeneous solution resulted which required generally from a half hour to an hour. Then at room temperature 25.6 g., 0.2 mole, of dichloroacetamide was added to the above mixture in several portions, the last of which was rinsed into the reaction flask with 50 ml. of trifluoroacetic acid, after which the mixture was stirred for an hour at room temperature. Then 32 g., 0.2 mole, of chilled bromine dissolved in 50 ml. of anhydrous trifluoroacetic acid were added dropwise over a two hour period. The reaction mixture was stirred for one hour after the addition of bromine was complete. The reaction mixture was then filtered to remove the silver bromide which was washed with three 25 ml. portions of chilled, anhydrous trifluoroacetic acid. The filtrate and wash solutions were combined and then distilled at room temperature and a pressure of 10 mm. The excess bromine and the trifluoroacetic acid were collected in a large trap which was cooled in a dry ice and isopropyl alcohol bath. As the solvent was being removed a white solid slowly separated from the reaction solution. When approximately three-fourths of the solvent had been removed the distillation was stopped and the solid was separated by filtration. This solid was dried under vacuum and recrystallized from carbon tetrachloride to give a product in the form of white needles which had a melting point of 95-95.5°C. The melting point reported (67) for N-bromodichloroacetamide is 96°C. Complete removal of the solvent from the filtrate at room temperature and a pressure of 10 mm. gave a yellow solid residue. This residue on recrystallization from carbon tetrachloride gave a colorless product in the form of needles which had a melting point of 95-95.5°C. The combined solids, pure N-bromodichloroacetamide, which weighed 33.5 g., 0.16 mole, represented an 81 per cent yield based on the amount of dichloroacetamide used. The bromine content determined for this material was 38.66 per cent. The calculated bromine content of N-bromodichloroacetamide is 38.63 per cent.

Preparation of N-Bromotrichloroacetamide in the Dark

Into a one liter, two neck flask fitted with a condenser and stirrer was placed 200 ml. of anhydrous trifluoroacetic acid and 23.0 g., 0.1 mole, of silver oxide. This mixture was cooled slightly and stirred until a homogeneous solution resulted. This generally required a half hour to an hour. Then at room temperature 32.0 g., 0.2 mole, of trichloroacetamide was added in several portions, the last of which was rinsed into the reaction flask with 50 ml. of trifluoroacetic acid. This mixture was stirred for one hour, at room temperature, after the addition of the amide was completed. Then 32 g., 0.2 mole, of chilled bromine dissolved in 50 ml. of anhydrous trifluoroacetic acid were added dropwise over a two hour period. The reaction mixture was stirred for one hour after the addition of the bromine was complete. The reaction mixture was then filtered to remove the silver bromide which was washed with three 25 ml. portions of chilled, anhydrous trifluoroacetic acid. The filtrate and wash solutions were combined and then distilled at room temperature and a pressure of 10 mm. The trifluoroacetic acid and excess bromine were collected in a large trap which was cooled in a dry ice and isopropyl alcohol bath. As the solvent was being removed a white solid slowly separated from the reaction solution. When approximately two thirds of the solvent has been removed the distillation was stopped and the solid was separated by filtration. This solid was dried under vacuum and recrystallized from carbon tetrachloride to give a white crystalline product in the form of needles which had a melting point of 123-123.5°C. The melting point reported (67) for N-bromotrichloroacetamide is 125°C. Complete removal of the solvent from the filtrate at room temperature and 10 mm. pressure gave a yellow colored solid residue. This residue was recrystallized from carbon tetrachloride to give a colorless crystalline product in the form of needles which had a melting point of 123-123.5°C. The combined solids, pure N-bromotrichloroacetamide, which weighed 38.5 g., 0.16 mole, represented an 80 per cent yield based on the amount of trichloroacetamide used. The bromine content determined for this material was 33.11 per cent. The calculated bromine content is 33.12 per cent.

Attempted Preparation of N-Bromoethoxyacetamide in the Dark

Into a one liter, two neck flask fitted with a condenser and stirrer were placed 200 ml. of anhydrous trifluoroacetic acid and 23.0 g., 0.1 mole, of silver oxide. This mixture was cooled slightly and stirred until a homogeneous solution resulted. This required one hour. Then at room temperature 20.6 g., 0.2 mole, of ethoxyacetamide was added in several portions, the last of which was rinsed into the reaction flask with 50 ml. of anhydrous trifluoroacetic acid. This mixture was stirred for one hour at room temperature. Then 32 g., 0.2 mole, of chilled bromine dissolved in 50 ml. of anhydrous trifluoroacetic acid were added dropwise over a two hour period. The reaction mixture was stirred for one hour after the addition of the bromine solution was complete. The reaction solution was a very dark red in color at this point, and it appeared as though a considerable amount of the bromine had not reacted. The reaction mixture was then filtered to remove the silver bromide which was washed with three 25 ml. portions of chilled, anhydrous trifluoroacetic acid. The filtrate and wash solutions were combined and then distilled at room temperature and 10 mm. pressure. The trifluoroacetic acid and excess bromine were collected in a large trap which was cooled in a dry ice and isopropyl alcohol bath. This procedure failed to cause any insoluble material to separate from the reaction mixture. The distillation was then continued at 1 mm. pressure for a half day which gave only an oily residue. The residual oil was taken up in carbon tetrachloride, but

Attempted Preparation of N-Bromoethoxyacetamide in the Dark

Into a one liter, two neck flask fitted with a condenser and stirrer were placed 200 ml. of anhydrous trifluoroacetic acid and 23.0 g., 0.1 mole, of silver oxide. This mixture was cooled slightly and stirred until a homogeneous solution resulted. This required one hour. Then at room temperature 20.6 g., 0.2 mole, of ethoxyacetamide was added in several portions, the last of which was rinsed into the reaction flask with 50 ml. of anhydrous trifluoroacetic acid. This mixture was stirred for one hour at room temperature. Then 32 g., 0.2 mole, of chilled bromine dissolved in 50 ml. of anhydrous trifluoroacetic acid were added dropwise over a two hour period. The reaction mixture was stirred for one hour after the addition of the bromine solution was complete. The reaction solution was a very dark red in color at this point, and it appeared as though a considerable amount of the bromine had not reacted. The reaction mixture was then filtered to remove the silver bromide which was washed with three 25 ml. portions of chilled, anhydrous trifluoroacetic acid. The filtrate and wash solutions were combined and then distilled at room temperature and 10 mm. pressure. The trifluoroacetic acid and excess bromine were collected in a large trap which was cooled in a dry ice and isopropyl alcohol bath. This procedure failed to cause any insoluble material to separate from the reaction mixture. The distillation was then continued at 1 mm. pressure for a half day which gave only an oily residue. The residual oil was taken up in carbon tetrachloride, but

colored solution the pressure began to rise slowly to 30 mm. and the solution turned a dark red color. It appeared as though some decomposition was taking place. This dark red oil was found to contain only a trace of active bromine and was discarded.

Analytical Reagents

The sodium hydroxide solution used in this work was standardized against potassium acid phthalate.

The hydrochloric acid solution used in this work was standardized against a standard solution of sodium hydroxide.

The standard sodium chloride solution used in this work was prepared by weighing a sample of Baker analytical grade sodium chloride, dissolving it in distilled water and diluting to the proper volume in a calibrated volumetric flask.

The silver nitrate solution used in this work was standardised against a standard sodium chloride solution.

The sodium thiosulfate solution used in this work was standardised against a weighed sample of potassium bromate.

Analytical Procedures

Iodimetric Method for the Determination of Active Bromine in N-Bromoamides and Imides (21)

Into a one quarter liter iodination flask were placed 5 ml. of glacial acetic acid and 60 ml. of a freshly prepared 4 per cent aqueous solution of potassium iodide. An accurately weighed sample of the N-bromoamide or imide was then added to the iodination flask and the few remaining particles of sample were washed into the flask with three 10 ml. portions of potassium iodide solution. The neck of the iodination flask was then washed with a few ml. of the potassium iodide solution. The flask was stoppered and a few drops of the potassium iodide solution were placed around the edge of the stopper. The flask was then agitated until all of the N-bromoamide or imide had dissolved.

The stopper was removed and the walls of the flask were washed down with a fine stream of water from a wash bottle. The solution was then titrated to a starch end-point with a standard 0.1N sodium thiosulfate solution.

To correct for any errors due to impurities in the glacial acetic acid or potassium iodide, a blank determination was made in exactly the same experimental procedure but without added N-bromoamide or imide. Results were calculated using the formula,

$$\frac{7.992 \times \text{ml. } S_2O_3^{=} \times \text{Normality } S_2O_3^{=}}{2 \times \text{wt. Sample}} = \text{per cent active bromine}$$

Experimental Techniques Employed to Account for All of the Bromine in the Reaction Between the N-Bromoamide and Toluene

The reaction, in the absence of light,[b] between the N-bromoamides and toluene at $80\pm0.1^\circ$C. was carried to completion as indicated by the absence of a color formation when a drop of the reaction mixture was

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[b] The thermostatic bath and reaction flask were protected against light by covering the apparatus with lightproof black cloth.

tested with an aqueous starch and potassium iodide solution. The reaction flask was then stoppered, cooled in the refrigerator for several hours, and filtered through a buchner funnel to remove the white precipitate. To insure against possible vapor loss the filter flask was cooled in a dry ice and isopropyl alcohol bath and an additional trap, cooled in the same way, was placed between the filter flask and the aspirator. The solid was washed twice with chilled carbon tetrachloride. The filtrate and combined washings were distilled at atmospheric pressure to remove completely the carbon tetrachloride and most of the excess toluene.

The residual solution remaining in the distillation flask was cooled and 20 ml. of benzyl alcohol was added, to serve as a chaser during the distillation of the monobrominated toluenes. The solution was then vacuum distilled using a 30 cm. vigreux column fitted with a distillation head. The material boiling at temperatures up to 93°C./10 mm., the boiling point of benzyl alcohol, was collected in a weighed receiver. The distillation was stopped when a drop from the delivery tip of the distillation head gave no precipitate with an alcoholic silver nitrate solution. Weighed samples were taken from the weighed distillate and weighed residue of the distillation for analysis for total halogen, active halogen and amide.

Total Halogen (76)

Samples of the distillate weighing approximately 1 g. and samples of the residual solution from the distillation weighing approximately

2 g. were rinsed into a quarter liter flat bottom flasks with 25 ml. of 99 per cent isopropyl alcohol. Two grams of sodium metal, cut into eight pieces were added and the mixture was kept just at its reflux temperature for three hours. Excess sodium metal was destroyed by adding water dropwise through the condenser. A 50 ml. quantity of water was added to the solution and after cooling it was neutralised to a phenolphthalein end point with 6N nitric acid followed by titration with standard 0.1N silver nitrate solution. Eosin was used as the indicator and 10 ml. of a 2 per cent dextrin solution was added to keep the silver bromide precipitate in a colloidal suspension, thus affording a sharp end point. The volume multiplied by the normality of the standard silver nitrate solution gave the total number of milliequivalents of bromide in the sample.

Active Halogen, Benzyl Bromide

Samples of the distillate, weighing approximately 3 g., were rinsed with 25 ml. of 99 per cent isopropyl alcohol into quarter liter, flat bottom flasks. A 50 ml. quantity of 1N sodium hydroxide solution was added and the solution was kept at its reflux temperature for two hours, after which it was cooled and neutralized with 6N nitric acid to a phenolphthalein end point. Following this the solution was titrated with standard 0.1N silver nitrate to an eosin endpoint. The volume multiplied by the normality of the standard silver nitrate solution gave the number of milliequivalents of active bromine in the sample.

Unseparated Amide

The necessity of analyzing the unseparated amide was determined by the nature of the amide. That is, any unseparated amides containing halogen, such as monochloroacetamide, would certainly be found in the residue of the distillation and possibly in the distillate. Due to the nature of the methods employed in analyzing for total and active halogen, the presence of chloroamides would effect the results of the total halogen and possibly the active halogen. Thus, by determining the amount of unseparated amide a correction could be made for the halogen in the amide. When no halogen was present in the amide such a determination was not necessary.

Samples of the distillate weighing approximately 3 g. and samples of the residue from the distillation weighing approximately 5 g. were rinsed into separate one quarter liter flat bottom flasks with 25 ml. of 99 per cent isopropyl alcohol. Each flask was set up for distillation in such a manner that the delivery tube of the distillation head extended beneath the surface of a 50 ml. quantity of freshly prepared, chilled, four per cent, boric acid solution contained in the receiver flask. Fifty ml. of a 0.5N sodium hydroxide solution was added to the distilling flask and the solution was distilled for one half hour. The boric acid solution containing the distillate and a blank boric acid solution were then titrated with standard 0.01N hydrochloric acid solution. The indicator solution was a freshly prepared mixture of methyl red and methylene blue in a ten to one ratio. The first appearance of a red color was taken as the end point.

The difference in the volume of the standard hydrochloric acid solution required for the blank and the sample was the volume of standard acid required to neutralize the ammonia produced by hydrolysis of the amide. The volume multiplied by the normality of the standard hydrochloric acid solution gave the number of milliequivalents of ammonia from the amide. A multiple of the number of milliequivalents of ammonia found, corresponding to the number of halogens in the amide, was the correction applied for the halogen of the amide.

Fortunately, no amide was found in the distillate and, therefore, no correction for active halogen had to be applied in this case. The amount of amide found in the residue was used as a correction for the total halogen.

The reaction, in the absence of light, between the N-bromoamides and toluene at 40.0°C. was allowed to proceed for twenty-four hours, at which point the reaction was always incomplete. The reaction solution at this time was colored a dark red and was immediately wrapped in black photographic paper and cooled in the refrigerator for several hours. The solid was separated by filtration in the dark into a filter flask connected to a trap cooled in an isopropyl alcohol and dry ice bath as described previously. The solid was dried for two hours in this manner and then transferred to a half liter volumetric flask where it was partially dissolved by filling the flask to the proper volume with carbon tetrachloride. The insoluble material was the amide which has a low solubility in the solvent. The unreacted N-bromoamide totally dissolved in the carbon tetrachloride and the resultant solution had an orange red color. An aliquot of this solution was shaken with 5 ml. of glacial acetic acid and 100 ml. of a freshly prepared four per cent potassium iodide solution. The liberated iodine was titrated with standard 0.1N sodium thiosulfate solution and from the volume of the latter solution used the amount of unreacted N-bromoamide could be calculated.

An alternative method for determining the amount of unreacted N-bromoamide was to dry and weigh the original precipitate of amide. This solid was then ground and samples were weighed, and the amount of unreacted N-bromoamide was determined iodimetrically as outlined above. This method, however, was not as reliable as the one previously described.

The filtrate from the N-bromoamide toluene reaction mixture was always a dark red color. It was observed in the earlier experiments that while this solution was being distilled to remove the carbon tetrachloride and excess toluene the dark red color disappeared and fumes of hydrogen bromide were observed. This suggested that unreacted, molecular bromine was present. To determine the amount of unreacted bromine which had been produced during the course of the reaction the filtrate was transferred in the dark into a distilling flask, and the filter flask and trap were rinsed with carbon tetrachloride which was added to the original filtrate. This solution was distilled in the dark under vacuum by means of a water aspirator and an oil bath at 40°C. The distillate was collected in a receiver, cooled in a dry ice and isopropyl alcohol bath. Distillation was continued until all of the carbon tetrachloride and most of the excess toluene had been collected. The red colored distillate was transferred in the dark to a quarter liter volumetric flask. Care had to be exercised in transferring this solution to the volumetric flask as several times a reaction occurred with a simultaneous loss of color and evolution of hydrogen bromide. The solution was diluted to the volume mark of the volumetric flask and then aliquots were taken and analyzed iodimetrically according to the above described method. The volume multiplied by the normality of the standard 0.1N sodium thiosulfate solution used gave the number of milliequivalents of free bromine.

The remainder of the determinations carried out for reactions at 40°C. for total halogen, active halogen and unseparated amide were done using the same experimental procedure employed for the corresponding determinations for the reactions at 80°C.

In some of the very early experiments diphenyl ether was used as the chaser instead of benzyl alcohol in the distillation of the monobrominated products. The use of diphenyl ether was discontinued because some of the unseparated amide was found in the distillate and there was the further possibility that any dibrominated toluenes, if formed, would also be carried over in the distillation.

The analytical methods used for total halogen, active halogen, and unseparated amide were carried out on known mixtures to demonstrate the applicability of the methods. A mixture containing 1.132 g., 6.98 milliequivalents, of trichloroacetamide; 1.81 g., 10.61 milliequivalents, of benzyl bromide; 2.046 g., 11.98 milliequivalents, of ortho bromotoluene; 1.520 g., 8.89 milliequivalents, of parabromotoluene; and 20 ml. of benzyl alcohol was analyzed in the manner described above. The distillate was analyzed for total halogen, active halogen and amide. The residual solution from the distillation was analyzed for total halogen and amide. The analytical results are summarized in Table X.

TABLE X[a]

SUMMARY OF QUANTITATIVE DETERMINATION OF BROMINE IN A MIXTURE CONSISTING OF BENZYL BROMIDE, o AND p-BROMOTOLUENE, TRICHLOROACETAMIDE AND BENZYL ALCOHOL

	Taken	Found in Distillate	Found[b] in Residue	Correction in Halogen Due to Amide	Net Bromide Found
Benzyl Bromide	10.61	10.59	—	0.00	10.59
Benzyl Bromide and Bromotoluenes	31.48	31.45	0.00	0.00	31.45
Trichloroacetamide	6.98	0.00	6.99	—	—

[a] All data expressed in milliequivalents.

[b] The residue was analyzed since the reaction between the N-bromoamides and toluene always gave some polybrominated toluenes which would be found in the residue of the distillation. By analyzing the non-distillable residue for halogen a good material balance for total bromide was obtained.

Reaction of N-Bromotrichloroacetamide with Toluene in the Dark at 80°±0.1°C.

Into a quarter liter, two neck flask, covered with an opaque black cloth, and fitted with a stirrer, reflux condenser and immersed

in a constant 80±0.1°C. bath were placed exactly 12.07 g., 0.05 mole, of N-bromotrichloroacetamide and exactly 50 ml., 0.47 mole, of toluene. The heterogeneous mixture was stirred at a constant rate throughout the course of the reaction. At each half hour interval one drop of the reaction mixture was removed and tested with a freshly prepared aqueous starch iodide solution. The reaction was complete in two and a half hours as evidenced by a negative test with the starch iodide indicator. The flask was removed from the oil bath, stoppered and set aside in the refrigerator overnight. The cold reaction mixture was filtered and the precipitated amide washed twice with cold carbon tetrachloride according to the methods described previously. The white solid had the same melting point as trichloroacetamide, 139-140°C., and a mixed melting point of it with an authentic sample of trichloroacetamide showed no depression. The weight of the trichloroacetamide was 7.500 g., 0.046 mole, a 92.5 per cent recovery of the amide.

The filtrate and wash solutions were combined, distilled and analyzed according to the methods outlined in detail previously.

The 0.05 mole of N-bromotrichloroacetamide are equal to 50 milliequivalents as a brominating agent.

<u>Analysis of Distillate:</u>

Total halogen (benzyl bromide and bromotoluenes)	45.63 milliequivalents
Active halogen (benzyl bromide)	21.75 milliequivalents
Unseparated Amide (ammonia)	0.00 milliequivalents

Analysis of Residue:

Total halogen (chloroamide, polybrominated toluene)	7.54 milliequivalents
Unseparated Amide (ammonia)	1.213 milliequivalents

Interpretation of Analyses:

Distillate:

The 45.63 milliequivalents of total halogen represented a 91.3 per cent conversion to monobrominated product.

The 21.75 milliequivalents of active halogen represent a 47.7 per cent side chain bromination based on the amount of monobrominated product.

Residue:

The 1.213 milliequivalents of unseparated trichloroacetamide represent 3.64 milliequivalents of halogen.

The total halogen found was 7.54 milliequivalents which when corrected for the halogen from the amide left a net of 3.90 milliequivalents of polybrominated toluene.

The combined total bromine was 49.53 milliequivalents which was a 99.1 per cent material balance.

Reaction of N-Bromotrichloroacetamide with Toluene in the Dark at 40°±0.1°C.

Into a quarter liter, two neck flask, covered with opaque black cloth, which was fitted with a stirrer and reflux condenser and immersed in a 40±0.1°C. bath were placed exactly 12.07 g., 0.05 mole, of N-bromotrichloroacetamide and exactly 50 ml., 0.47 mole, of toluene.

The heterogeneous mixture was stirred at a constant rate during a reaction period of exactly twenty-four hours. The flask was removed from the bath, stoppered, wrapped in black photographic paper and set aside in the refrigerator overnight. The solution was filtered in the dark to remove the precipitate. The distillate and all evolved vapors were caught in a filter flask and trap both of which were cooled in a dry ice and isopropyl alcohol bath. The solid was dried as much as possible in this manner and then by means of a vacuum pump. The precipitate, in this case, was not washed with carbon tetrachloride because of the solubility of any unreacted N-bromoamide in this solvent. Tje solid was transferred to a 250 ml. volumetric flask where it was dissolved in carbon tetrachloride. The resultant solution was analyzed for unreacted N-bromotrichloroacetamide.

The reddish brown colored filtrate was rinsed from the filter flask and trap with carbon tetrachloride into a distilling flask. The distillation was carried out in the dark according to the methods already described. The free bromine, carbon tetrachloride and toluene were caught in a receiver cooled in a dry ice and isopropyl alcohol bath. The distillate was transferred to a volumetric flask, diluted to the volume mark with carbon tetrachloride and the amount of free bromine determined iodimetrically. The liquid residue from this distillation was then distilled under vacuum to separate the monobrominated toluene using benzyl alcohol as a chaser.

Analyses:

Unreacted N-Bromotrichloroacetamide	0.47 milliequivalents
Free Bromine	2.59 milliequivalents

Analysis of Distillate:

Total Halogen (benzyl bromide and bromotoluene)	34.17 milliequivalents
Active Halogen (benzyl bromide)	5.05 Milliequivalents
Unseperated Amide (ammonia)	0.00 milliequivalents

Analysis of Residue:

Total Halogen (trichloroacetamide and polybrominated toluene)	9.95 milliequivalents
Unseperated Amide (ammonia)	1.54 milliequivalents

Interpretation of Analyses:

The 0.05 mole of N-bromoamide corresponds to 50 milliequivalents as a brominating agent and 100 milliequivalents as an oxidizing agent. Thus, the 0.47 milliequivalents of unreacted N-bromoamide as determined iodimetrically were equivalent to 0.24 milliequivalents as a brominating agent. The reaction was 99.5 per cent complete based on the disappearance of the N-bromoamide.

Distillate:

The 34.17 milliequivalents of total halogen represents a 68.3 per cent conversion to monobrominated toluene based on the 50 milliequivalents of N-bromoamide which were used.

The 5.05 milliequivalents of benzyl bromide represent a 14.8 per cent side chain bromination based on the 34.17 milliequivalents of monobrominated product.

Residue:

The 1.54 milliequivalents of trichloroacetamide found in the residue contain 4.62 milliequivalents of halogen. The total halogen found in the residue was 9.95 milliequivalents, which when corrected for the halogen of the amide left a net of 5.33 milliequivalents of polybrominated toluene.

The combined total bromine from all analyses was 42.33 milliequivalents which was an 84.7 per cent material balance. The possible sources of error causing a low material balance in this reaction and all reactions run at 40°C. which were not carried to completion could arise from loss of bromine during the vacuum distillation, entrapment of bromotoluene or benzyl bromide in the solid which was not washed with carbon tetrachloride because of the solubility of the unreacted N-bromoamide, and decomposition of the unreacted N-bromoamide giving free bromine before the unreacted N-bromoamide could be analysed.

Reaction of N-Bromodichloroacetamide with Toluene in the Dark at 80°± 0.1°C.

Employing exactly the same procedure as in the previous reaction at 80°C., 10.34 g., 0.05 mole, of N-bromodichloroacetamide was allowed to react with exactly 50 ml., 0.47 mole, of toluene. The reaction was complete in six hours as indicated by a negative test with a starch iodide solution.

The analysis of the reaction mixture was carried out exactly as described previously. The solid obtained weighed 5.210 g. and was a mixture of dichloroacetamide and a very small amount, < 0.1 g., of a substance which sublimed above 200°C. This high melting substance contained 13.75 per cent nitrogen and 79.90 per cent halogen. Its structure was unidentified. The major portion of the solid had the same melting point as dichloroacetamide, 97-98°C., and had a mixed melting point with authentic dichloroacetamide of 97-98°C.

Analysis of Distillate:

Total Halogen (benzylbromide and bromotoluene)	44.89 milliequivalents
Active Halogen (benzyl bromide)	22.22 milliequivalents
Unseparated Amide (ammonia)	0.00 milliequivalents

Analysis of Residue:

Total Halogen (dichloroacetamide and polybrominated toluene)	8.22 milliequivalents
Unseparated Amide (ammonia)	1.80 milliequivalents

Interpretation of Analyses:

Distillate:

The 44.89 milliequivalents of total halogen represented an 89.8 per cent conversion to monobrominated product.

The 22.22 milliequivalents of benzyl bromide represented a 49.7 per cent side chain bromination based on the amount of monobrominated product.

Residue:

The 1.80 milliequivalents of unseparated dichloroacetamide represented 3.60 milliequivalents of halogen. The total halogen

found was 8.22 milliequivalents which when corrected for the halogen from the amide left a net of 4.62 milliequivalents of polybrominated toluene.

The combined total bromine was 49.51 milliequivalents which was a 99.8 per cent material balance.

Reaction of N-Bromodichloroacetamide with Toluene in the Dark at 80 ± 0.1° C.

In exactly the same manner as previously described for the reaction of an N-bromoamide with toluene 10.34 g., 0.05 mole, of N-bromodichloroacetamide was allowed to react with exactly 50 ml., 0.47 mole of toluene for exactly twenty-four hours. The reaction was not complete and the reaction mixture had a dark red color. It was filtered as described above and the solid was dissolved in carbon tetrachloride. The filtrate was distilled under vacuum in the manner previously described.

Analyses:

Unreacted N-bromodichloroacetamide	36.61 milliequivalents
Free Bromine	2.73 milliequivalents

Analysis of Distillate:

Total Halogen (benzyl bromide and bromotoluene)	17.12 milliequivalents
Active Halogen (benzyl bromide)	4.28 milliequivalents
Unseparated Amide (ammonia)	0.00 milliequivalents

Analysis of Residue:

Total Halogen (dichloroacetamide and polybrominated toluene)	5.03 milliequivalents
Unseparated Amide (ammonia)	0.00 milliequivalents

Interpretation of Analyses:

The 0.05 mole of N-bromodichloroacetamide correspond to 50 milliequivalents as a brominating agent and 100 milliequivalents as an oxidizing agent. Thus, the 36.61 milliequivalents of unreacted N-bromoamide as determined iodimetrically were equivalent to 18.31 milliequivalents as a brominating agent. The reaction was 63.4 per cent complete based on the amount of unrecovered N-bromodichloroacetamide.

Distillate:

The 17.12 milliequivalents of total halogen represented a 54.1 per cent conversion to monobrominated product based on the amount of unrecovered N-bromoamide.

The 4.28 milliequivalents of benzyl bromide represented a 25.0 per cent side chain bromination based on the amount of monobrominated product.

Residue:

Since no amide was found in the residue the 5.03 milliequivalents of total halogen found represented the amount of polybrominated toluene.

The combined total bromine from all the analyses was 43.19 milliequivalents which represented an 86.4 per cent material balance. The possible sources of error leading to a low material balance were discussed previously.

Reaction of N-Bromomonochloroacetamide with Toluene in the Dark at 80°±0.1°C.

In the experimental manner described previously 8.621 g., 0.05

mole, of N-bromomonochloroacetamide was allowed to react with exactly 50 ml., 0.47 mole, of toluene. The reaction was completed in twelve hours as indicated by a negative test with a starch iodide solution.

A white solid was filtered from the cooled reaction mixture. This solid weighed 4.54 g., 0.048 mole, and had the same melting point as chloroacetamide, 119-120°C. A mixed melting point of this solid with authentic monochloroacetamide was 119-120°C.

Analysis of Distillate:

Total Halogen (benzyl bromide and bromotoluene)	39.39 milliequivalents
Active Halogen (benzyl bromide)	35.89 milliequivalents
Unseparated amide (ammonia)	0.00 milliequivalents

Analysis of Residue:

Total Halogen (chloroacetamide and polybrominated toluene)	10.16 milliequivalents
Unseparated amide (ammonia)	0.00 milliequivalents

Interpretation of Analyses:

Distillate:

The 39.39 milliequivalents of total halogen represented a 78.8 per cent conversion to monobrominated product.

The 35.89 milliequivalents of benzyl bromide represented a 91.1 per cent side chain bromination based on the amount of monobrominate product.

Residue:

Since no amide was found in the residue the 10.16 milliequivalents of halogen represented the amount of polybrominated toluene.

The combined total bromine from all analyses was 49.55 milliequivalents which represented a 99.1 per cent material balance.

Reaction of N-Bromomonochloroacetamide with Toluene in the Dark at 40° ± 0.1° C.

In exactly the same manner as previously described for the reaction of an N-bromoamide with toluene 8.621 g., 0.05 mole, of N-bromomonochloroacetamide was allowed to react with exactly 50 ml., 0.47 mole, of toluene for exactly twenty-four hours. The reaction was not complete and the reaction mixture had a dark red color. The chilled reaction mixture was filtered as in previous cases already described and the solid dissolved in carbon tetrachloride. The filtrate was distilled under vacuum.

Analyses:

Unreacted N-Bromomonochloroacetamide	84.06 milliequivalents
Free Bromine	0.79 milliequivalents

Analysis of Distillate:

Total Halogen (benzyl bromide and bromotoluene)	5.27 milliequivalents
Active Halogen (benzyl bromide)	2.54 milliequivalents
Unseparated Amide (ammonia)	0.00 milliequivalents

Analysis of Residue:

Total Halogen (monochloroacetamide and polybrominated toluene)	1.71 milliequivalents
Unseparated Amide (ammonia)	0.00 milliequivalents

Interpretation of Analyses:

The 0.05 mole of N-bromomonochloroacetamide corresponded to 50 milliequivalents as a brominating agent and 100 milliequivalents as an oxidizing agent. Thus, the 84.06 milliequivalents of unreacted N-bromoamide as determined iodimetrically were equivalent to 42.03 milliequivalents as a brominating agent. The reaction was 15.9 per cent complete based on the amount of unrecovered N-bromomonochloroacetamide.

Distillate:

The 5.27 milliequivalents of total halogen represented a 69.6 per cent conversion to monobrominated product based on the amount of unrecovered N-bromoamide.

The 2.54 milliequivalents of benzyl bromide represented a 48.3 per cent side chain bromination based on the amount of monobrominated product.

Residue:

Since no amide was found in the residue the 1.71 milliequivalents of total halogen found represented the amount of polybrominated toluene.

The combined total bromine from all the analyses was 49.80 milliequivalents or a material balance of 98.6 per cent.

Reaction of Bromine with Toluene in the Dark at 80°±0.1°C.

In the manner described previously 1.25 ml., 0.0244 mole, of bromine was allowed to react with exactly 50 ml., 0.47 mole, of toluene.

The reaction was completed in four and a half hours as indicated by a negative test with a starch iodide solution. The reaction mixture was then distilled at atmospheric pressure to remove all of the hydrogen bromide and most of the toluene. Benzyl alcohol was added and the reaction mixture distilled under vacuum as previously described.

Analysis of Distillate:

Total Halogen (benzyl bromide and bromotoluene)	23.25 milliequivalents
Active Halogen (benzylbromide)	21.81 milliequivalents

Analysis of Residue:

Total Halogen (polybrominated toluene)	0.61 milliequivalents

Interpretation of Analyses:

The 1.25 ml., 0.0244 mole, of bromine corresponded to 24.38 milliequivalents as a brominating agent.

Distillate:

The 23.25 milliequivalents of total halogen represented a 95.6 per cent conversion to monobrominated product based on the amount of bromine consumed in the reaction.

The 21.81 milliequivalents of benzyl bromide represented a 93.7 per cent side chain bromination based on the amount of monobrominated product.

Residue:

There was 0.61 milliequivalent of polybrominated toluene in the residue.

The combined total bromine from all the analyses was 23.86 milliequivalents which was a material balance of 98.2 per cent.

Reaction of Bromine with Toluene in the Dark at 40°±0.1°C.

In exactly the same manner as described previously 1.25 ml., 0.0244 mole, of bromine was allowed to react with exactly 50 ml., 0.47 mole, of toluene. The reaction was completed in ten and a half hours as indicated by a negative test with a starch iodide solution. The reaction mixture was then distilled at atmospheric pressure to remove all of the hydrogen bromide and most of the toluene. Benzyl alcohol was then added and the reaction mixture distilled under vacuum as previously described.

Analyses of Distillate:

Total Halogen (benzyl bromide and bromotoluene)	23.26 milliequivalents
Active Halogen (benzyl bromide)	20.69 milliequivalents

Analysis of Residue:

Total Halogen (polybrominated toluene)	0.72 milliequivalents

Interpretation of Analyses:

The 1.25 ml., 0.0244 mole, of bromine corresponded to 24.38 milliequivalents as a brominating agent.

Distillate:

The 23.26 milliequivalents of total halogen represented a 95.6 per cent conversion to monobrominated product based on the amount of bromine consumed in the reaction.

The 20.69 milliequivalents of benzyl bromide represented an 89.0 per cent side chain bromination based on the amount of monobrominated product.

Residue:

There was 0.72 milliequivalent of polybrominated toluene in the residue.

The combined total bromine from all of analyses was 23.98 milliequivalents which corresponds to a material balance of 98.5 per cent.

The bromination experiments carried out are summarized, at 80°C., in Table VI, and, at 40°C., in Table VII.

Decomposition of the N-Bromoamides

The photochemical decomposition of the N-bromoamides was investigated with the objective of being able to determine the relative rates of formation of free bromine, presumably by a free radical type of reaction, involving such compounds. It was anticipated that such information would be of aid in the elucidation of the over-all mechanism of the Wohl Ziegler reaction.

Photochemical Decomposition of N-Bromoamides

Three experimental methods were utilized in these studies. Decomposition, (a) by means of a simple tungsten lamp with a focusing lens and no filter, (b) by means of a mercury lamp using a 350-550 millimicron filter and a focusing lens, and (c) by means of a somewhat more elaborate system in which the light source was a mercury lamp

cooled by means of an air fan. A transformer was used to insure that a constant voltage was being supplied to the mercury lamp. The light was passed through a focusing lens, a 438 millimicron interference filter, a rectangular hole cut through a metal shield and finally through a ground glass Beckmann cell containing the sample being irradiated.

In all of the above methods the equipment was mounted on an optical bench at properly spaced intervals such that the maximum obtainable light intensity was available to the sample.

In the third method, (c) an additional feature was the use of a mirror mounted adjacent to the focusing lens in such a manner as to reflect some of the stray light from the mercury lamp source onto a photomultiplier tube. A record of the electromotive force generated was kept on a continuous recorder. This data was used primarily to check as to the constant intensity of the light falling on the sample during long periods of irradiation.

The sample was irradiated for varying lengths of time and after each known time interval the spectrum of the sample was scanned from 280 to 540 millimicrons by means of a Beckmann D.U. spectrophotometer. A hydrogen lamp source was used in the range 280 through 315 millimicrons and a tungsten lamp in the 320 to 540 millimicron range. A fixed slit width was used for each wave length.

The bromine absorption peak for a solution of bromine in carbon tetrachloride was reported (77) to be at 415 millimicrons. Thus, by irradiating a solution of an N-bromoamide in carbon tetrachloride of known concentration for definite lengths of time and following the formation of free bromine by means of the Beckman D.U. spectrophotometer the relative rates of decomposition of the bromoamides could be determined.

The results of the photochemical decompositions are summarized in Figures XVI through XIX.

Figure XVIII shows the Beers Law curves, optical density versus concentration, for a solution of bromine in carbon tetrachloride at various wave lengths in the spectrum.

Figure XIX is a plot of the optical density versus wave length for an N-bromotrichloroacetamide solution, 9.19×10^{-3} M, in carbon tetrachloride as a result of irradiation by method (b). The lengths of time of irradiation for each curve are given in Table XI.

Figure XVI is a plot of the optical density versus time for the 415 millimicron bromine band arising from the decomposition of the N-bromotrichloroacetamide solution, 9.19×10^{-3} M, in carbon tetrachloride according to method (b).

Figure XVII curve A is a plot of the optical density versus time for the 415 millimicron bromine band arising from the decomposition of an N-bromotrichloroacetamide solution, 9.32×10^{-3} M, in carbon tetrachloride according to method (c).

Figure XVII curve B is a plot of the optical density versus time for the 415 millimicron band arising from the decomposition, by method (c), of a carbon tetrachloride solution, 8.39×10^{-3} M, in

N-bromotrichloroacetamide and 4.66×10^{-4} M in bromine, which represents a total of $9.32 \times 10^{-}$ M gram atomic weights of bromine.

It was observed during the course of photochemical decomposition that the spectrum of solutions of the N-bromoamides which were only slightly decomposed as a result of irradiation showed little or no increase in the extent of decomposition after being set aside in the dark overnight.

However, those solutions which were decomposed sufficiently so that a bromine absorption band was present showed a further significant decomposition when, set aside in the dark overnight.

The photochemical decomposition was discontinued when it was realised that the light sources used were not strong enough to induce decomposition at a reasonable rate. The tungsten lamp gave no significant decomposition in two days. Ground glass Beckman cells were used to hold the samples which were being irradiated. However, it was observed during lengthy itradiations that losses of bromine due to evaporation had occurred. Furthermore, in the decomposition of N-bromotrichloroacetamide, 9.19×10^{-3} M, shown in Figure XIX, the theoretical amount of bromine which could have been liberated, 4.60×10^{-3} M, was not realised. The maximum concentration of bromine attained was 3.60×10^{-3} M and on further irradiation this value decreased to 3.48×10^{-3} M. This decrease could only have occurred through an evaporation loss. However, there is a strong possibility that with other brominating agents which have an active hydrogen that self bromination can occur. This self bromination would be aided by the slow rate of decomposition and by the light source used for the decomposition. This would also lead to a decrease in the amount of free bromine and a loss through formation of hydrogen bromide.

However, several significant observations could be made. A study of Figure XIX indicates that the first appearance of a bromine peak was at 380 millimicrons rather than at the 415 millimicrons as reported (77). As the decomposition proceeds the peak gradually shifts to longer wave lengths until it was at 400 millimicrons, at which point no further decomposition was observed. In the decomposition of a mixture of bromine and N-bromotrichloroacetamide, Figure XVII curve B, the original peak was at 415 millimicrons. However, as the decomposition proceeded the peak shifted to shorter wave lengths and reached a low of 405 millimicrons.

Figure XVII also shows that the presence of bromine catalyzes the decomposition of the N-bromoamide. The shape of the curve in Figure XVI suggests bromine catalysis and the further observation that decomposition continues in the presence of bromine when irradiation has ceased again suggests bromine catalysis in such decompositions.

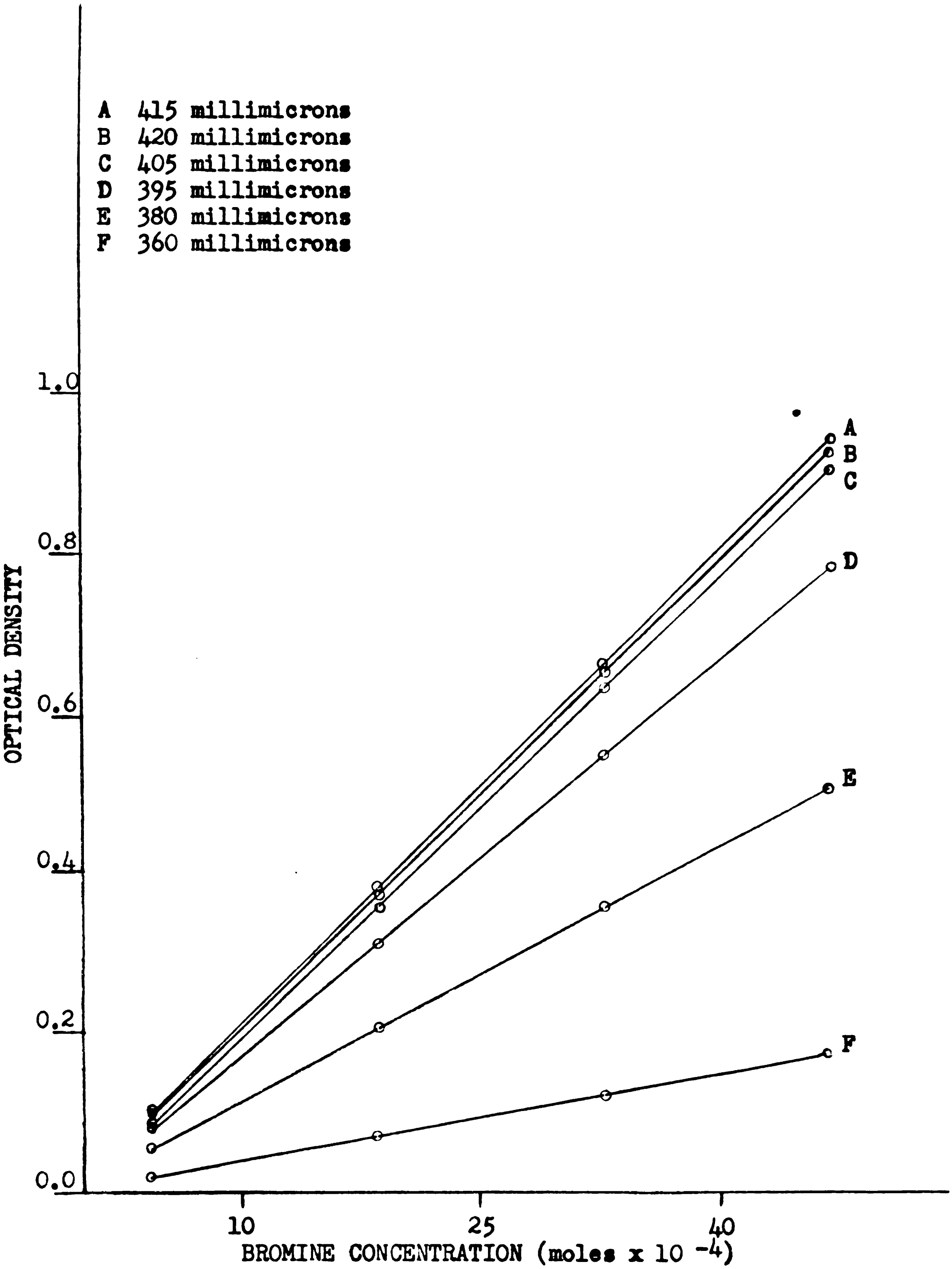

FIGURE XVIII. OPTICAL DENSITY VERSUS CONCENTRATION OF BROMINE AT DIFFERENT WAVE LENGTHS

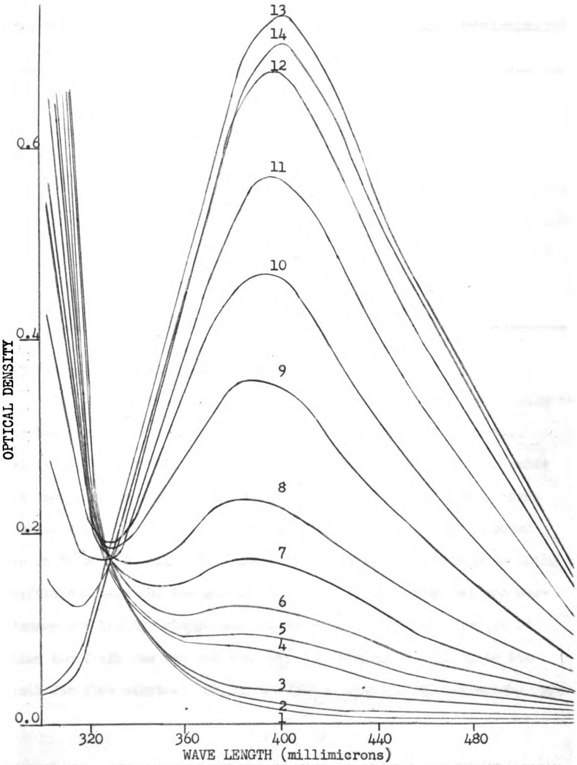

FIGURE XIX. OPTICAL DENSITY VERSUS WAVE LENGTH FOR THE DECOMPOSITION OF N-BROMOTRICHLOROACETAMIDE DURING VARYING PERIODS OF IRRADIATION

TABLE XI

LENGTH OF TIME OF IRRADIATION FOR THE DECOMPOSITION OF THE BROMOTRICHLOROACETAMIDE

Curve Number	Time in Minutes
1	0
2	76
3	209
4	408
5	470
6	618
7	810
8	1062
9	1602
10	2109
11	2617
12	3448
13	4748
14	5384

Thermal Decomposition of N-Bromoamides

The thermal decomposition of the N-bromo mono, di, and trichloroacetamides was investigated at 80°C. for varying time intervals. Fifty ml. of a solution, of known concentration of the N-bromoamide in carbon tetrachloride, was placed in a 100 ml. single neck round bottom flask. The flask was fitted with a condenser and immersed in an 80°±0.1°C. oil bath. After five minutes of immersion to allow sufficient time for the air in the system to be driven out the condenser was tightly stoppered. At the end of a definite length of time the flask was removed from the oil bath and placed in an ice bath for five minutes. All of the above experimental operations were

carried out in the dark. The spectrum of the solution was then scanned from 300 to 540 millimicrons in the manner described previously.

The results of these experiments were not reproducable. At one time a given sample would decompose rapidly; whereas, a short time later the decomposition of the same solution proceeded quite slowly. Undoubtedly some loss by evaporation had occurred, but in addition to this oxygen and surface catalysis played an important role. The difference in rates of decomposition of the same sample was not caused by impurities in the sample since the N-bromoamide had been recrystallized and analyzed immediately prior to use. A more refined method of decomposing the amides in the absence of oxygen and surface catalysis is required to obtain a quantitative estimate of the relative rates of decomposition of the N-bromoamides.

However, several observations could be made from the thermal decompositions of the N-bromoamides. The peak for a solution of bromine in carbon tetrachloride was reported (77) to be at 415 millimicrons. However, in the thermal decomposition of the N-bromo mono, di, and trichloroacetamides the first appearance of a bromine peak was at 380 millimicrons. The position of this peak gradually shifted to longer wave lengths during the decomposition and reached a maximum of between 405 and 410 millimicrons. This was similar to the observation made in the photochemical decomposition. The thermal decomposition of a solution of N-bromodichloroacetamide and bromine in carbon tetrachloride showed an initial peak, before decomposition, at 415 millimicrons. During the decomposition this peak gradually shifted downward until it reached a minimum of 405 millimicrons. This, again, is similar to the observation made during the photochemical decomposition of a solution of N-bromotrichloroacetamide and bromine in carbon tetrachloride.

Solutions of the three N-bromoamides in carbon tetrachloride were prepared and set aside in closed vessels in the ordinary room light. The first to develop a bromine color was the N-bromomonochloroacetamide, and the last to develop such a color was N-bromotrichloroacetamide.

Solutions of the three N-bromoamides in chloroform were set aside in closed vessels for a period of two months. In a relatively short time a bromine color appeared in the solution, but after a longer period of time it disappeared and a small amount of a white crystalline solid was present on the bottom of the flasks. The analyses of these solids were as follows:

Solution in Chloroform of	Per Cent Nitrogen	Per Cent Chlorine
N-Bromomonochloroacetamide	15.24	77.74
N-Bromodichloroacetamide	15.13	77.05
N-Bromotrichloroacetamide	14.01	77.67

All of the solids sublimed above 200°C. and did not melt. Their structures were unknown and the calculated nitrogen and chlorine values for the corresponding azo compounds which might have arisen as a result of the decomposition of the N-bromoamide are lower than the above values.

A white crystalline solid containing 18.05 per cent nitrogen was obtained from the thermal decomposition of a solution of N-bromomonochloroacetamide in carbon tetrachloride. The amount of solid, 1.240 mgs., was insufficient to permit a halogen analysis.

The molar extinction coefficient for the carbonyl band of the three N-bromoamides in carbon tetrachloride were determined and are recorded in Table XII.

TABLE XII

MOLAR EXTINCTION COEFFICIENT FOR THE CARBONYL BAND OF SOME N-BROMOAMIDES IN CARBON TETRACHLORIDE

Compound	Molar Extinction Coefficient
N-Bromomonochloroacetamide	372
N-Bromodichloroacetamide	430
N-Bromotrichloroacetamide	455

SUMMARY

SUMMARY

N-bromosuccinimide and N,N'-dibromodimethylhydantoin were reacted with cyclohexene in carbon tetrachloride and chloroform. In carbon tetrachloride the N-bromosuccinimide gave the higher yield, 63 per cent versus 55 per cent, of allylic bromination product, 3-bromocyclohexene. In chloroform only bromine addition occurred.

Nitrogen sulfide tetrabromide, $N_4S_4Br_4$, and phosphonitrilic bromide, $PNBr_2$, were prepared and reacted with cyclohexene. The former gave some allylic bromination, but bromine addition was the main reaction. The latter gave no organic bromine products.

The N-bromo mono, di, and trichloroacetamides were prepared by adding bromine to their silver salts in trifluoroacetic acid as a reaction solvent. Attempts to prepare N-bromoacetamide, N-bromoethoxyacetamide and N-bromophylacetamide by the same method were unsuccessful.

The N-bromo mono, di and trichloroacetamides were allowed to react with toluene at two temperatures, 40°C. and 80°C. The N-bromomonochloroacetamide gave the highest ratio of side chain to ring bromination, and the N-bromotrichloroacetamide gave the lowest ratio.

The photochemical and thermal decompositions of the N-bromoamides were investigated. It was found that bromine catalyzed the decomposition and that the bromine formed during the decomposition was complexed.

A mechanism including the heterolytic and homolytic dissociation of the nitrogen bromine bond was proposed, based on a correlation between the infrared, decomposition and bromination data.

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APPENDIX

TABLE XIII

INFRARED ABSORPTION DATA FOR ACETAMIDE

Solvent $CHCl_3$ - 9.920×10^{-3} M, Base Line 90% of Transmission

Wave Length		Solvent		Solution		Net (Carbonyl)
u	V	%T	$\log_e I_o/I \cdot 10^3$	%T	$\log_e I_o/I \cdot 10^3$	$\log_e I_o/I \cdot 10^3$
5.700	1754	89	11	88	22	11
5.710	1751	89	11	88	22	11
5.720	1748	89	11	88	22	11
5.730	1745	89	11	88	22	11
5.740	1742	89	11	88	22	11
5.750	1739	89	11	88	22	11
5.760	1736	90	00	88	22	22
5.770	1733	89	11	88	22	11
5.780	1730	90	00	88	22	22
5.790	1727	90	00	87	33	33
5.800	1724	90	00	85	57	57
5.810	1721	90	00	84	69	69
5.820	1718	90	00	82	93	93
5.830	1715	90	00	80	117	117
5.840	1712	90	00	75	182	182
5.850	1709	90	00	70	252	252
5.860	1706	90	00	66	310	310
5.870	1704	90	00	64	341	341
5.880	1701	90	00	63	357	357
5.890	1698	90	00	66	310	310
5.900	1695	90	00	70	252	252
5.910	1692	90	00	70	252	252
5.920	1689	90	00	70	252	252
5.930	1686	90	00	68	280	280
5.940	1684	90	00	61	389	389
5.950	1681	90	00	54	511	511
5.960	1678	90	00	48	629	629
5.970	1675	90	00	49	609	609
5.980	1672	90	00	54	511	511
5.990	1669	90	00	65	325	325
6.000	1667	90	00	70	252	252
6.010	1664	90	00	76	168	168
6.020	1661	90	00	80	117	117
6.030	1658	90	00	82	93	93
6.040	1656	89	11	82	93	82
6.050	1653	90	00	85	57	57
6.060	1650	90	00	85	57	57
6.070	1647	90	00	86	46	46
6.080	1645	90	00	85	57	57
6.090	1642	90	00	85	57	57
6.100	1639	89	11	85	57	46
6.110	1637	89	11	85	57	46
6.120	1634	89	11	86	46	35
6.130	1631	89	11	86	46	35
6.140	1629	88	22	86	46	24
6.150	1626	87	33	86	46	13

TABLE XIV

INFRARED ABSORPTION DATA FOR PROPIONAMIDE

Solvent $CHCl_3$ - 1.513 x 10^{-2} M, Base Line 90% of Transmission

Wave Length u	Wave Length V	Solvent %T	Solvent $\log_e I_o/I \cdot 10^3$	Solution %T	Solution $\log_e I_o/I \cdot 10^3$	Net (Carbonyl) $\log_e I_o/I \cdot 10^3$
5.750	1739	88	22	86	46	24
5.760	1736	88	22	86	46	24
5.770	1733	88	22	86	46	24
5.780	1730	88	22	86	46	24
5.790	1727	89	11	85.5	52	41
5.800	1724	89.5	6	85.5	52	46
5.810	1721	89.5	6	85	57	51
5.820	1718	89	11	84	69	57
5.830	1715	89	11	83	80	69
5.840	1712	90	00	82	93	93
5.850	1709	90	00	80	117	117
5.860	1706	90	00	76	168	168
5.870	1704	90	00	71	237	237
5.880	1701	89.5	6	66	310	304
5.890	1698	89.5	6	56	474	468
5.900	1695	90	00	51	567	567
5.910	1692	90	00	43	738	738
5.920	1689	90	00	38	862	862
5.930	1686	89	11	37	889	878
5.940	1684	89	11	37	889	878
5.950	1681	89.5	6	37	889	883
5.960	1678	89.5	6	42	762	756
5.970	1675	90	00	47	650	650
5.980	1672	89	11	53	529	518
5.990	1669	89	11	59	422	411
6.000	1667	89.5	6	67.5	288	281
6.010	1664	89.5	6	69.5	259	253
6.020	1661	90	00	75	182	182
6.030	1658	89.5	6	77	156	150
6.040	1656	87.5	28	77	156	128
6.050	1653	87.5	28	77	156	128
6.060	1650	88	22	80	117	95
6.070	1647	88	22	79	130	108
6.080	1645	89	11	81	105	94
6.090	1642	89	11	82	93	82
6.100	1639	88	22	81	105	83
6.110	1637	87.5	28	80.5	111	83
6.120	1634	87	33	81.5	99	66
6.130	1631	87.5	28	82	93	65
6.140	1629	87.5	28	80.5	111	83
6.150	1626	87	33	80.5	111	78
6.160	1623	86.5	40	80	117	77

TABLE XV

INFRARED ABSORPTION DATA FOR ETHOXYACETAMIDE IN CHLOROFORM

Solvent 1.048 x 10^{-3} M, Base Line 90% of Transmission

Wave Length u	V	Solvent %T	$\log_e I_o/I \cdot 10^3$	Solution %T	$\log_e I_o/I \cdot 10^3$	Net (Carbonyl) $\log_e I_o/I \cdot 10^3$
5.700	1754	89	11	88	22	11
5.710	1751	89	11	87	33	22
5.720	1748	89	11	87	33	22
5.730	1745	89	11	87	33	22
5.740	1742	89	11	87	33	22
5.750	1739	89	11	86	46	35
5.760	1736	90	00	86	46	46
5.770	1733	89	11	85	57	46
5.780	1730	90	00	85	57	57
5.790	1727	90	00	84	69	69
5.800	1724	90	00	84	69	69
5.810	1721	90	00	82	93	93
5.820	1718	90	00	80	117	117
5.830	1715	90	00	80	117	117
5.840	1712	90	00	79	130	130
5.850	1709	90	00	77	156	156
5.860	1706	90	00	74	196	196
5.870	1704	90	00	70	252	252
5.880	1701	90	00	65	325	325
5.890	1698	90	00	57	456	456
5.900	1695	90	00	52	549	549
5.910	1692	90	00	43	738	738
5.920	1689	90	00	42	762	762
5.930	1686	90	00	42	762	762
5.940	1684	90	00	47	650	650
5.950	1681	90	00	56	474	474
5.960	1678	90	00	61	389	389
5.970	1675	90	00	67	295	295
5.980	1672	90	00	74	196	196
5.990	1669	90	00	78	142	142
6.000	1667	90	00	82	93	93
6.010	1664	90	00	83	80	80
6.020	1661	90	00	84	69	69
6.030	1658	90	00	85	57	57
6.040	1656	89	11	84	69	58
6.050	1653	90	00	84	69	69
6.060	1650	90	00	84	69	69
6.070	1647	90	00	85	57	57
6.080	1645	90	00	86	46	46
6.090	1642	90	00	87	33	33
6.100	1639	89	11	86	46	35
6.110	1637	89	11	86	46	35
6.120	1634	89	11	86	46	35
6.130	1631	89	11	86	46	35
6.140	1629	88	22	86	46	24
6.150	1626	87	33	86	46	13
6.160	1623	87	33	85	57	24

TABLE XVI

INFRARED ABSORPTION DATA FOR ETHOXYACETAMIDE IN CARBON TETRACHLORIDE

1.437×10^{-3} M, Base Line 90% of Transmission

Wave Length µ	ν	Solvent %T	Solvent $\log_e I_0/I \cdot 10^3$	Solution %T	Solution $\log_e I_0/I \cdot 10^3$	Net (Carbonyl) $\log_e I_0/I \cdot 10^3$
5.700	1754	90	00	86.5	40	40
5.710	1751	89.5	6	86	46	40
5.720	1748	89	11	85	57	46
5.730	1745	89.5	6	85	57	51
5.740	1742	89.5	6	84	69	63
5.750	1739	89.5	6	84	69	63
5.760	1736	89	11	82	93	82
5.770	1733	89	11	80	117	106
5.780	1730	89.5	6	76	168	162
5.790	1727	90	00	71	237	226
5.800	1724	89.5	6	69	265	259
5.810	1721	89.5	6	65	325	319
5.820	1718	89	11	63	357	346
5.830	1715	89.5	6	59	422	416
5.840	1712	90	00	52	549	549
5.850	1709	89	11	46	671	660
5.860	1706	89	11	42	762	751
5.870	1704	89	11	39	837	826
5.880	1701	88	22	39	837	820
5.890	1698	88.5	17	38	862	845
5.900	1695	89.5	6	47	650	644
5.910	1692	89.5	6	54	511	505
5.920	1689	89.5	6	63	357	351
5.930	1686	88.5	17	67	295	278
5.940	1684	89.5	6	75	182	176
5.950	1681	89.5	6	77	156	150
5.960	1678	89	11	78	142	131
5.970	1675	89	11	79	130	119
5.980	1672	89	11	79	130	119
5.990	1669	89	11	82	93	82
6.000	1667	88.5	17	82	93	76
6.010	1664	88.5	17	82	93	76
6.020	1661	88.5	17	83	80	63
6.030	1658	88.5	17	83	80	63
6.040	1656	87	33	82	93	60
6.050	1653	87	33	82	93	60
6.060	1650	87	33	82	93	60
6.070	1647	87.5	28	82	93	66
6.080	1645	87	33	84	69	36
6.090	1642	86	46	83	80	34
6.100	1639	85	57	82	93	36

TABLE XVII

INGRARED ABSORPTION DATA FOR CHLOROACETAMIDE

Solvent $CHCl_3$ - 1.295 x 10^{-2}M, Base Line 90% of Transmission

Wave Length		Solvent		Solution		Net (Carbonyl)
u	V	%T	$\log_e I_o/I \cdot 10^3$	%T	$\log_e I_o/I \cdot 10^3$	$\log_e I_o/I \cdot 10^3$
5.700	1754	89	11	88	22	11
5.710	1751	89	11	87	33	22
5.720	1748	88	22	87	33	11
5.730	1745	89	11	87	33	22
5.740	1742	89	11	87	33	22
5.750	1739	89	11	86	46	35
5.760	1736	89	11	85	57	46
5.770	1733	89	11	84	69	58
5.780	1730	89	11	82	93	82
5.790	1727	90	00	80	117	117
5.800	1724	89	11	78	142	131
5.810	1721	90	00	78	142	142
5.820	1718	90	00	77	156	156
5.830	1715	90	00	76	168	168
5.840	1712	90	00	75	182	182
5.850	1709	90	00	71	237	237
5.860	1706	90	00	66	310	310
5.870	1704	90	00	58	440	440
5.880	1701	90	00	50	588	588
5.890	1698	90	00	41	786	786
5.900	1695	90	00	36	916	916
5.910	1692	90	00	35	945	945
5.920	1689	90	00	41	786	786
5.930	1686	90	00	50	588	588
5.940	1684	90	00	65	325	325
5.950	1681	90	00	70	252	252
5.960	1678	90	00	74	196	196
5.970	1675	90	00	78	142	142
5.980	1772	90	00	80	117	117
5.990	1669	90	00	84	69	69
6.000	1667	90	00	84	69	69
6.010	1664	90	00	84	69	69
6.020	1661	90	00	84	69	69
6.030	1658	90	00	85	57	57
6.040	1656	90	00	85	57	57
6.050	1653	90	00	85	57	57
6.060	1650	89	11	85	57	46
6.070	1647	90	00	85	57	57
6.080	1645	90	00	86	46	46
6.090	1642	90	00	86	46	46
6.100	1639	89	11	85	57	46

TABLE XVIII

INFRARED ABSORPTION DATA FOR DICHLOROACETAMIDE IN CHLOROFORM

1.172 x 10^{-2} M, Base Line 90% of Transmission

Wave Length		Solvent		Solution		Net (Carbonyl)
u	V	%T	$\log_e I_0/I \cdot 10^3$	%T	$\log_e I_0/I \cdot 10^3$	$\log_e I_0/I \cdot 10^3$
5.650	1770	88.5	17	86	46	29
5.660	1767	89	11	86	46	35
5.670	1764	89	11	86.5	40	29
5.680	1761	89	11	85	57	46
5.690	1757	89	11	85	57	46
5.700	1754	89	11	85	57	46
5.710	1751	88	22	84.5	62	41
5.720	1748	88	22	84.5	63	41
5.730	1745	88.5	17	84.5	63	46
5.740	1742	89	11	82.5	87	76
5.750	1739	89	11	81	105	94
5.760	1736	89	11	79	130	119
5.770	1733	89	11	76	168	157
5.780	1730	89	11	70	252	241
5.790	1727	90	00	63	357	357
5.800	1724	90	00	54	511	511
5.810	1721	90	00	45	693	693
5.820	1718	90	00	40	811	811
5.830	1715	90	00	40	811	811
5.840	1712	90	00	41	786	786
5.850	1709	90	00	49	609	609
5.860	1706	90	00	58	440	440
5.870	1704	90	00	68	280	280
5.880	1701	90	00	74	196	196
5.890	1698	89	11	78	142	131
5.900	1695	90	00	82	93	93
5.910	1692	90	00	83	80	80
5.920	1689	90	00	84	69	69
5.930	1686	90	00	83	80	80
5.940	1684	90	00	84	69	69
5.950	1681	89.5	6	85	57	51
5.960	1678	89.5	6	85	57	51
5.970	1675	89.5	6	85	57	51
5.980	1672	90	00	86	46	46
5.990	1669	90	00	85	57	57
6.000	1667	90	00	86	46	46
6.010	1664	90	00	86.5	40	40

TABLE XIX

INFRARED ABSORPTION DATA FOR DICHLOROACETAMIDE IN CARBON TETRACHLORIDE

		9.960×10^{-3} M, Base Line 90% of Transmission				
Wave Length		Solvent		Solution		Net (Carbonyl)
u	V	%T	$\log_e I_o/I \cdot 10^3$	%T	$\log_e I_o/I \cdot 10^3$	$\log_e I_o/I \cdot 10^3$
5.600	1786	89.5	6	88	22	17
5.610	1783	90	00	88	22	22
5.620	1779	89.5	6	88	22	17
5.630	1776	89.5	6	88	22	17
5.640	1773	90	00	87.5	28	28
5.650	1770	90	00	88	22	22
5.660	1767	90	00	87.5	28	28
5.670	1764	90	00	86.5	40	40
5.680	1761	90	00	86.5	40	40
5.690	1757	90	00	86	46	46
5.700	1754	90	00	85.5	52	52
5.710	1751	90	00	84	69	69
5.720	1748	90	00	83	80	80
5.730	1745	90	00	82	93	93
5.740	1742	90	00	80	117	117
5.750	1739	89.5	6	77.5	149	143
5.760	1736	90	00	73	209	209
5.770	1733	90	00	64	341	341
5,780	1730	90	00	53.5	520	520
5.790	1727	89.5	6	46	671	665
5.800	1724	90	00	46	671	671
5.810	1721	89	11	47.5	640	629
5.820	1718	90	00	55	494	494
5.830	1715	90	00	67	295	295
5.840	1712	89.5	6	73	209	203
5.850	1709	89.5	6	76.5	162	156
5.860	1706	89	11	79	130	119
5.870	1704	89.5	6	80.5	111	105
5.880	1701	89	11	82	93	82
5.890	1698	89.5	6	82	93	87
5.900	1695	89.5	6	84.5	63	57
5.910	1692	88.5	17	83.5	75	58
5.920	1689	87.5	28	83.5	75	46
5.930	1686	88.5	17	82.5	87	70
5.940	1684	88.5	17	85	57	40
5.950	1681	88	22	84.5	63	41
5.960	1678	87.5	28	84.5	63	35
5.970	1675	87.5	28	84.5	63	35
5.980	1672	88.5	17	84	69	52

TABLE XX

INFRARED ABSORPTION DATA FOR TRICHLOROACETAMIDE

Solvent $CHCl_3$ – 1.013 x 10^{-2} M, Base Line 90% Transmission

Wave Length μ	ν	%T	Solvent $\log_e I_o/I\cdot10^3$	%T	Solution $\log_e I_o/I\cdot10^3$	Net (Carbonyl) $\log_e I_o/I\cdot10^3$
5.600	1786	89	11	88	22	11
5.610	1783	89	11	88	22	11
5.620	1779	89	11	87	33	22
5.630	1776	89	11	87	33	22
5.640	1773	89	11	87	33	22
5.650	1770	89	11	87	33	22
5.660	1767	89	11	87	33	22
5.670	1764	89	11	87	33	22
5.680	1761	89	11	84	69	58
5.690	1757	89	11	83	80	69
5.700	1754	89	11	81	105	94
5.710	1751	89	11	79	130	119
5.720	1748	89	11	76	168	157
5.730	1745	89	11	70	252	241
5.740	1742	89	11	62	373	362
5.750	1739	89	11	56	474	463
5.760	1736	90	00	51	567	567
5.770	1733	89	11	48	629	618
5.780	1730	90	00	48	629	629
5.790	1727	90	00	51	567	567
5.800	1724	90	00	56	474	474
5.810	1721	90	00	63	357	357
5.820	1718	90	00	70	252	252
5.830	1715	90	00	76	168	168
5.840	1712	90	00	82	93	93
5.850	1709	90	00	83	80	80
5.860	1706	90	00	85	57	57
5.870	1704	90	00	86	46	46
5.880	1701	90	00	86	46	46
5.890	1698	90	00	86	46	46
5.900	1695	90	00	86	46	46
5.910	1692	90	00	88	22	22
5.920	1689	90	00	88	22	22
5.930	1686	90	00	88	22	22
5.940	1684	90	00	88	22	22
5.950	1681	90	00	88	22	22
5.960	1678	90	00	88	22	22

TABLE XXI

INFRARED ABSORPTION DATA FOR TRIFLUOROACETAMIDE

Solvent $CHCl_3$ - 1.082 x 10^{-2}M, Base Line 90% of Transmission

Wave Length		Solvent		Solution		Net (Carbonyl)
u	V	%T	$\log_e I_o/I \cdot 10^3$	%T	$\log_e I_o/I \cdot 10^3$	$\log_e I_o/I \cdot 10^3$
5.550	1802	89	11	85.5	52	41
5.560	1799	89	11	85.5	52	41
5.570	1795	89	11	85	57	46
5.580	1792	88	22	85	57	35
5.590	1789	89	11	84.5	63	52
5.600	1786	88	22	83.5	75	53
5.610	1783	88	22	83	80	58
5.620	1779	88	22	82	93	71
5.630	1776	88	22	80.5	111	89
5.640	1773	88	22	78	142	120
5.650	1770	88	22	74.5	189	167
5.660	1767	88	22	69	265	243
5.670	1764	88	22	65	325	303
5.680	1761	88	22	57	456	434
5.690	1757	88	22	52	549	527
5.700	1754	88.5	17	45	693	676
5.710	1751	88	22	43.5	726	704
5.720	1748	88	22	43.5	726	704
5.730	1745	88	22	45	693	671
5.740	1742	88	22	52	549	527
5.750	1739	88	22	58.5	431	408
5.760	1736	88	22	65	325	303
5.770	1733	88	22	72	223	201
5.780	1730	90	00	78	142	142
5.790	1727	90	00	80.5	111	111
5.800	1724	90	00	81.5	99	99
5.810	1721	90	00	82	93	93
5.820	1718	90	00	82	93	93
5.830	1715	90	00	84	69	69
5.840	1712	90	00	85	57	57
5.850	1709	90	00	84.5	63	63
5.860	1706	90	00	84.5	63	63
5.870	1704	90	00	84.5	63	63
5.880	1701	90	00	85	57	57
5.890	1698	90	00	86	46	46
5.900	1695	90	00	86	46	46

TABLE XXII

INFRARED ABSORPTION DATA FOR BENZAMIDE

Solvent $CHCl_3$ - 9.147 x 10^{-3} M, Base Line 90% of Transmission

Wave Length u	V	Solvent %T	Solvent $\log_e I_o/I \cdot 10^3$	Solution %T	Solution $\log_e I_o/I \cdot 10^3$	Net (Carbonyl) $\log_e I_o/I \cdot 10^3$
5.750	1739	88	22	87.5	28	6
5.760	1736	88.5	17	87.5	28	11
5.770	1733	88	22	87.5	28	6
5.780	1730	90	00	89	11	11
5.790	1727	89	11	88	22	11
5.800	1724	89	11	87.5	28	17
5.810	1721	89	11	87.5	28	17
5.820	1718	89	11	86	46	35
5.830	1715	89	11	87.5	28	17
5.840	1712	89.5	6	87.5	28	23
5.850	1709	90	00	87.5	28	28
5.860	1706	89.5	6	86	46	40
5.870	1704	89	11	86	46	35
5.880	1701	88.5	17	84	69	52
5.890	1698	88	22	80	117	95
5.900	1695	88	22	76	168	146
5.910	1692	89	11	71	237	226
5.920	1689	89	11	64	341	330
5.930	1686	89	11	59	422	411
5.940	1684	89	11	52	549	538
5.950	1681	89	11	47	650	639
5.960	1678	89	11	45	693	682
5.970	1675	89	11	48	629	618
5.980	1672	89	11	52	549	538
5.990	1669	89	11	62	373	362
6.000	1667	89	11	68	280	269
6.010	1664	89	11	73	209	198
6.020	1661	89	11	78.5	136	125
6.030	1658	89	11	81	105	94
6.040	1656	88.5	17	80	117	100
6.050	1653	88	22	85	57	35
6.060	1650	88	22	84.5	63	41
6.070	1647	87.5	28	84	69	41
6.080	1645	87.5	28	85	57	29
6.090	1642	88	22	84.5	63	41
6.100	1639	88	22	84.5	63	41
6.110	1637	88	22	84.5	63	41
6.120	1634	87.5	28	84.5	63	35
6.130	1631	87.5	28	84.5	63	35
6.140	1629	86.5	40	84.5	63	23
6.150	1626	86.5	40	84.5	63	23

TABLE XXIII

INFRARED ABSORPTION DATA FOR PHENYLACETAMIDE

Solvent $CHCl_3$ - 9.381×10^{-3} M, Base Line 90% of Transmission

Wave Length u	Wave Length V	Solvent %T	Solvent $\log_e I_o/I \cdot 10^3$	Solution %T	Solution $\log_e I_o/I \cdot 10^3$	Net (Carbonyl) $\log_e I_o/I \cdot 10^3$
5.750	1739	88	22	87	33	11
5.760	1736	88	22	87	33	11
5.770	1733	88	22	86.5	40	18
5.780	1730	88	22	86.5	40	18
5.790	1727	89	11	86.5	40	29
5.800	1724	89.5	6	86	46	40
5.810	1721	89.5	6	85.5	52	46
5.820	1718	89	11	84	69	58
5.830	1715	89	11	83.5	75	64
5.840	1712	90	00	83.5	75	75
5.850	1709	90	00	82.5	87	87
5.860	1706	90	00	80.5	112	112
5.870	1704	90	00	78.5	136	136
5.880	1701	89.5	6	75.5	175	169
5.890	1698	89.5	6	70.5	245	239
5.900	1695	90	00	66	310	310
5.910	1692	90	00	60.5	397	397
5.920	1689	90	00	56.5	465	465
5.930	1686	89	11	55	494	483
5.940	1684	89	11	54.5	503	492
5.950	1681	89.5	6	52	549	543
5.960	1678	89.5	6	51.5	558	552
5.970	1675	90	00	52.5	539	539
5.980	1672	89	11	55	494	483
5.990	1669	89	11	60.5	397	386
6.000	1667	89.5	6	69.5	259	253
6.010	1664	89.5	6	72	223	217
6.020	1661	90	00	79	130	130
6.030	1658	89.5	6	81	105	99
6.040	1656	87.5	28	81	105	77
6.050	1653	87.5	28	81	105	77
6.060	1650	88	22	82.5	87	65
6.070	1647	88	22	82.5	87	65
6.080	1645	89	11	85	57	46
6.090	1642	89	11	85	57	46
6.100	1639	88	22	85	57	35
6.110	1637	87.5	28	83.5	75	47
6.120	1634	87	33	86	46	13
6.130	1631	87.5	28	85.5	52	24
6.140	1629	87.5	28	85	57	29
6.150	1626	87	33	84.5	40	29

TABLE XXIV

INFRARED ABSORPTION DATA FOR N-BROMOMONOCHLOROACETAMIDE

Solvent CCl_4 - 8.664 x 10^{-3} M, Base Line 90% of Transmission

Wave Length		Solvent		Solution		Net (Carbonyl)
u	V	%T	$\log_e I_o/I \cdot 10^3$	%T	$\log_e I_o/I \cdot 10^3$	$\log_e I_o/I \cdot 10^3$
5.650	1770	90	00	89.5	6	6
5.660	1767	90	00	89	11	11
5.670	1764	90	00	88	22	22
5.680	1761	90	00	88.5	17	17
5.690	1757	90	00	88	22	22
5.700	1754	90	00	87.5	28	28
5.710	1751	90	00	87	33	33
5.720	1748	90	00	87	33	33
5.730	1745	90	00	86.5	40	40
5.740	1742	90	00	85.5	52	52
5.750	1739	89.5	6	84.5	63	57
5.760	1736	90	00	82.5	87	87
5.770	1733	90	00	81.5	99	99
5.780	1730	90	00	80.5	112	112
5.790	1727	89.5	6	78.5	136	130
5.800	1724	90	00	75	182	182
5.810	1721	89	11	71.5	230	219
5.820	1718	90	00	68	280	280
5.830	1715	90	00	64	341	341
5.840	1712	89.5	6	62.5	365	359
5.850	1709	89.5	6	64.5	333	327
5.860	1706	89	11	67.5	288	277
5.870	1704	89.5	6	69	265	259
5.880	1701	89	11	72	223	212
5.890	1698	89.5	6	74	196	190
5.900	1695	89.5	6	76.5	162	156
5.910	1692	88.5	17	78	142	125
5.920	1689	87.5	28	78.5	136	108
5.930	1686	88.5	17	80	117	100
5.940	1684	88.5	17	82	93	76
5.950	1681	88	22	82	93	70
5.960	1678	87.5	28	83	80	52
5.970	1675	87.5	28	84	69	41
5.980	1672	88.5	17	84	69	52
5.990	1669	88.5	17	86.5	46	23
6.000	1667	87.5	28	85.5	52	24
6.010	1664	88.5	17	86.5	40	23
6.020	1661	87.5	28	86	46	18
6.030	1658	86.5	40	86	46	6

TABLE XXV

INFRARED ABSORPTION DATA FOR N-BROMODICHLOROACETAMIDE

Solvent CCl_4 - 8.121 x 10^{-3} M, Base Line 90% of Transmission

Wave Length		Solvent		Solution		Net (Carbonyl)
u	V	%T	$\log_e I_0/I \cdot 10^3$	%T	$\log_e I_0/I \cdot 10^3$	$\log_e I_0/I \cdot 10^3$
5.600	1786	89.5	6	89	11	6
5.610	1783	89.5	6	89	11	6
5.620	1779	89.5	6	89	11	6
5.630	1776	89.5	6	89	11	6
5.640	1773	89.5	6	87.5	28	22
5.650	1770	89.5	6	87.5	28	22
5.660	1767	90	00	87.5	28	28
5.670	1764	90	00	87.5	28	28
5.680	1761	90	00	86	46	46
5.690	1757	90	00	86	46	46
5.700	1754	90	00	86.5	40	40
5.710	1751	90	00	86	46	46
5.720	1748	89.5	6	84	69	63
5.730	1745	89.5	6	83.5	75	69
5.740	1742	89.5	6	82	93	87
5.750	1739	89.5	6	79	130	124
5.760	1736	90	00	76.5	162	162
5.770	1733	90	00	73.5	203	203
5.780	1730	90	00	67	295	295
5.790	1727	90	00	62	373	373
5.800	1724	90	00	61.5	381	381
5.810	1721	89.5	6	65	325	319
5.820	1718	89	11	70	252	241
5.830	1715	89	11	75.5	175	164
5.840	1712	89.5	6	80	117	111
5.850	1709	90	00	80	117	117
5.860	1706	90	00	79	130	130
5.870	1704	90	00	81	105	105
5.880	1701	90	00	82	93	93
5.890	1698	90	00	85	57	57
5.900	1695	90	00	86	46	46
5.910	1692	90	00	86	46	46
5.920	1689	90	00	86	46	46
5.930	1686	89	11	86	46	35
5.940	1684	89	11	87.5	28	17
5.950	1681	89	11	87.5	28	17
5.960	1678	89	11	87.5	28	17
5.970	1675	89.5	6	88	22	17
5.980	1672	89.5	6	87.5	28	22
5.990	1669	89.5	6	88.5	17	11
6.000	1667	89.5	6	88.5	17	11

TABLE XXVI

INFRARED ABSORPTION DATA FOR N-BROMOTRICHLOROACETAMIDE

Solvent CCl_4 - 8.410×10^{-3} M, Base Line 90% of Transmission

Wave Length		Solvent		Solution		Net (Carbonyl)
u	V	%T	$\log_e I_o/I \cdot 10^3$	%T	$\log_e I_o/I \cdot 10^3$	$\log_e I_o/I \cdot 10^3$
5.550	1802	88	22	87.5	28	6
5.560	1799	88	22	87.5	28	6
5.570	1795	88.5	17	87.5	28	11
5.580	1792	88.5	17	87.5	28	11
5.590	1789	89	11	88.5	17	6
5.600	1786	89	11	88	22	11
5.610	1783	89	11	88.5	17	6
5.620	1779	89	11	88	22	11
5.630	1776	89	11	88	22	11
5.640	1773	89.5	6	87.5	28	22
5.650	1770	89	11	87.5	28	17
5.660	1767	89.5	6	86.5	40	34
5.670	1764	89.5	6	86	46	40
5.680	1761	89.5	6	85	57	51
5.690	1757	89.5	6	82	93	87
5.700	1754	90	00	78	142	142
5.710	1751	89.5	6	73	209	203
5.720	1748	89	11	66	310	299
5.730	1745	89.5	6	59	422	416
5.740	1742	89.5	6	57	456	450
5.750	1739	89.5	6	59	422	416
5.760	1736	89	11	65	325	314
5.770	1733	89	11	71	237	226
5.780	1730	89.5	6	79	130	124
5.790	1727	90	00	82	93	93
5.800	1724	89.5	6	83	80	74
5.810	1721	89.5	6	85	57	51
5.820	1718	89	11	85	57	46
5.830	1715	89.5	6	87	33	27
5.840	1712	90	00	88	22	22
5.850	1709	89	11	87.5	28	17
5.860	1706	89	11	87.5	28	17
5.870	1704	89	11	87.5	28	17
5.880	1701	88.5	17	88	22	6
5.890	1698	88.5	17	88	22	6
5.900	1695	89.5	6	88	22	17
5.910	1692	89.5	6	88	22	17
5.920	1689	89.5	6	88.5	17	11
5.930	1686	88.5	17	88	22	6
5.940	1684	89.5	6	88	22	17
5.950	1681	89.5	6	88.5	17	11

Date Due

AUG 4 '58			