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Direct and indirect determination of olefinic unsaturation with bromine

Garth Eugene Wood
Iowa State University

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DIRECT AND INDIRECT DETERMINATION OF

OLEFINIC UNSATURATION WITH BROMINE

by

Garth Eugene Wood

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INTRODUCTION

Determination of olefinic unsaturation falls into the general category of functional group analysis. The olefinic linkage or double bond consists of a strong σ bond and a weaker π bond. Double bonds are utilized in diverse ways by the synthetic chemist in the formulation of new compounds and in the development of new methods for making known compounds. The analytical chemist then is given the responsibility of quantitatively determining this double bond for at least two major reasons. First, he may be required to report how much of a certain olefinic compound is present because the olefinic portion per se is important. Second, the olefinic portion of a molecule may be a convenient way to analyze for a compound containing some other functional group.

The work described in this thesis was undertaken in an attempt to develop an improved method for the determination of olefinic unsaturation. A direct titration procedure utilizing a spectrophotometric end point and an indirect spectrophotometric method were developed. The direct method is useful for the analysis of relatively large amounts of unsaturation while small to trace amounts can be analyzed by the indirect method.

BACKGROUND

General

The importance of determining olefinic unsaturation and
the inherent difficulties associated with it have led a large
number of investigators to exploration in this field during
the past several decades. Because the double bond is commonly
found in molecules which display quite diverse structures and
substituents, a wide range of chemical reactivities and varia-
tions in physical properties are associated with it. These
facts essentially preclude the development of a simple, pre-
cise method for even a majority of compounds containing an
olefinic linkage. Interferences from within the particular
compound being determined and from sources outside it are
numerous. Side reactions can and do occur; many times with
unexpected and disheartening ease.

A wide variety of analytical methods exist for determin-
ing olefinic unsaturation. These include chemical methods and
instrumental methods. Polgár and Jungnickel (24) present a
broad picture of procedures developed prior to 1956. Since
that time most papers have dealt with attempts to improve on
existing techniques. Because the double bond does exhibit
such wide variation in chemical reactivity, much time and

effort has been devoted to the development of methods for determination of specific compounds or groups of compounds.

The typical reaction of the double bond is addition. Therefore, it is only logical that nearly all chemical methods of analysis of olefins utilize this reaction. Attack of the ethylenic linkage and subsequent formation of addition products by such things as halogens, hydrogen, peracids, potassium permanganate, nitrogen tetroxide, nitric acid, nitrosyl chloride, sulfuric acid, thiocyanogen, mercury salts, maleic anhydride, mercaptans, bisulfite, and amines have led to useful analytical methods involving these compounds.

Nearly all techniques developed for determination of olefinic unsaturation are volumetric in nature and depend on the measurement of the amount of reagent consumed in the addition reaction. The measurement of reaction products is the basis for a limited number. Probably the most important and widely used of these latter methods are the oxidative procedures involving eventual rupture of the double bond.

Some instrumental methods have been developed for quantitative determination of olefinic unsaturation. Infrared and Raman spectra provide qualitative and some quantitative information. Ultraviolet and visible absorption techniques have also been applied especially to conjugated systems. These

methods are generally somewhat limited in scope and will not be discussed further.

Chromatographic methods have also received some attention. These techniques are based on the partitioning of a particular compound or class of compounds between two different phases. The various components of a mixture thus separated must then be analyzed by some other means.

Procedures employing halogens for determination of olefinic unsaturation are numerous. Iodine, bromine, chlorine, iodine monobromide, and iodine monochloride have all been used to add to the double bond. Iodination techniques suffer from the fact that iodine is relatively unreactive toward the double bond. Consequently, it has found limited utility. Iodine monobromide and iodine monochloride have received some attention and because of their higher reactivity have more utility than iodine. Because of the high reactivity of chlorine, any attempt to quantitatively add it to the double bond is usually accompanied by sufficient substitution to render the procedure useless. Hence few addition methods utilize this halogen.

In 1881 Allen (1) described the determination of unsaturation in shale and petroleum products using bromine liberated by the action of hydrochloric acid on sodium hypobromite.

Since that time bromine has been widely used as a halogenation reagent for quantitative determination of the double bond. Many bromination procedures have been proposed, but as stated above the diversity of compounds containing double bonds prevents development of a universal bromination method. However, by controlling a number of the variables involved it is possible to adapt bromination procedures to a large variety of unsaturates and to obtain accurate quantitative information.

Mechanism

The reaction mechanism for the addition of bromine to a double bond is generally considered to be ionic and to consist of two steps. Fieser and Fieser (11, p. 149) show the initial step as electrophilic attack by the cation Br^+ derived from considering the bromine molecule to be an ion pair Br^+Br^-. Equation 1 shows this cation combining with the π electrons of the double bond to form an intermediate carbonium ion (a). This is generally accepted as the rate-determining step in the addition reaction. Neutralization of charge and formation of the dibromide (b) occur during the second step when the negatively charged Br^- ion is added.

$$\ce{>C=C< + Br+ -> \underset{(a)}{\overset{Br}{>C-\overset{+}{C}<}} \quad \overset{Br^-}{\rightharpoondown} \quad \underset{(b)}{\overset{Br}{>C-C<_{Br}}}} \tag{1}$$

It should be noted that other anions in solution such as those present as a result of dissociation of the solvent molecules may supplant the bromide ion in this second step. The overall reaction for solvents of water, acetic acid, alcohols, or mixtures of these compounds is given by Equation 2. The net result is the production of hydrobromic acid and the formation of the monobromo addition compound.

$$\ce{>C = C< + Br2 + HX -> >\overset{\displaystyle Br}{C} - \underset{\displaystyle X}{C}< + HBr} \tag{2}$$

$$(X = OH^-, CH_3COO^-, OR^-)$$

LITERATURE

Indirect Methods

Bromination methods for determination of unsaturation can conveniently be considered to consist of two distinct types, indirect and direct. Indirect procedures involve addition of an excess of bromine, a period of time for reaction, and determination of the unconsumed bromine. Direct procedures, as the name implies, involve direct titration of the unsaturated compound with bromine or with some other titrant which will produce bromine.

McIlhiney (19) used an indirect method for determination of unsaturation. His solvent was carbon tetrachloride, and he used an excess of standard bromine solution. The unconsumed bromine was determined by adding aqueous potassium iodide and titrating the liberated iodine with standard sodium thiosulfate. Hydrogen bromide, produced if substitution of bromine for hydrogen in the unsaturated compound takes place, was determined by adding iodate and determining the additional iodine liberated. A correction to account for the substitution which had occurred was then applied to the total bromine consumption figure.

Francis (12) used excess bromine liberated from aqueous

bromide-bromate in acid solution for the analysis of the olefinic content of petroleum products. An indirect iodometric method was again used to determine the unconsumed bromine.

Buckwalter and Wagner (6) used free bromine as the brominating species in their solvent of carbon tetrachloride. Because the presence of water enhances the spontaneous elimination of hydrogen bromide from the dibromide addition products, they employed a stream of nitrogen to transfer the unconsumed bromine and the hydrobromic acid from the reaction vessel into aqueous potassium iodide. The iodine thus liberated was titrated with standard sodium thiosulfate. They also attempted to correct for substitution by determining the hydrobromic acid produced during the reaction.

Lucas and Pressman (18) employed a mercury(II) sulfate catalyst in a solvent of water-acetic acid-carbon tetrachloride for determination of compounds containing double and triple bonds. They used a 15 to 20% excess of bromide-bromate solution and employed an indirect iodometric method for determining the unreacted bromine.

An indirect iodometric method for determination of the excess bromine was also used by Rowe, Furnas, and Bliss (26) in the determination of the iodine number of tall oil. Six-

teen hours reaction time and a mercury(II) acetate catalyst were used with pyridinium sulfate dibromide as the brominating agent. They reported no observable substitution to have taken place.

Miller and Pearman (21) determined ethylene by shaking the gas with excess bromine in glacial acetic acid. The excess bromine was then determined by indirect iodometry.

Low bromine absorption values were determined by Reid and Beddard (25) using an indirect method utilizing bromine in glacial acetic acid at ice water temperatures. Three minutes reaction time was allowed after which the excess bromine was determined by an indirect iodometric method.

Byrne and Johnsōn⁻ (7) reported an acid-catalyzed bromination for determination of unsaturation. They used an indirect method with a solvent system of methanol-water containing 10% or more sodium bromide and 0.4 to 2.0% hydrochloric acid. A standard bromide-bromate solution served as a source of bromine. Reaction times of from one to 120 minutes were allowed before the unconsumed bromine was determined utilizing indirect iodometry.

Polgár and Jungnickel (24, pp. 229-255) discuss a large number of indirect methods with many variations and applications. Solvents employed include acetic acid, chloroform,

carbon tetrachloride, water, methanol, and mixtures of these. The bromination reagents used in the procedures described include free bromine, tribromide ion, hydrogen perbromide complex in chloroform, pyridinium bromide perbromide, pyridine methylbromide dibromide, and bromine on carbon. Titanous chloride and arsenious acid have been used as alternatives to the indirect iodometric method for the determination of the unconsumed bromine. Mercury(II) salts added as solutions or as the dry salts have generally been used as catalysts.

Some inherent disadvantages are associated with indirect bromination methods in general. The time element involved is particularly undesirable. Reaction times are seldom less than one minute and sometimes are considerably longer even for those compounds which add bromine readily. It is then still necessary to determine the unconsumed bromine. Also the long reaction times and reagent excesses associated with indirect bromination procedures could lead to substitution errors although this point is moot.

Various attempts have been made to correct for this substitution. McIlhiney (19) assumed that all hydrobromic acid that was produced during the course of the bromination reaction came from substitution of bromine for hydrogen. He

attempted to correct total bromine absorption values for the
substitution which took place by determining the hydrobromic
acid produced.

Polgár and Jungnickel (24, pp. 230-231) list side effects
that may result in production of hydrobromic acid. Besides
substitution these include elimination of hydrogen bromide
from the addition product and reaction of the sample with the
solvent. They conclude that substitution corrections based on
acidity determinations are fundamentally incorrect.

Another method designed to correct results for substitu-
tion errors is described by Polgár and Jungnickel (24, p. 237).
This method is based on the assumption that the rate of addi-
tion is rapid initially, but gradually decreases and becomes
comparable to the slower rate of the substitution reaction. A
determination is made and followed by one or two additional
identical determinations at accurately measured increased reac-
tion times. If a significant increase in bromine consumption
occurs with the increased time, the results are extrapolated
back to zero time. This extrapolation should give the correct
addition value provided addition was complete when the first
value was obtained, and the rate of substitution is constant.

Indirect iodometric methods are the overwhelming choice

for the determination of the unconsumed bromine. However these techniques are subject to certain complications. Solubility considerations generally dictate that bromination reactions be performed in solvents containing no water or only a small percentage of water. At the same time the addition of potassium iodide and subsequent titration of the iodine liberated with standard sodium thiosulfate is performed in aqueous media. If the organic solvent is not miscible with water, cloudy or otherwise difficult to manage solutions result. Solvents miscible with water sometimes adversely affect the performance of the starch indicator used to facilitate visual location of the end point in the titration of iodine with sodium thiosulfate. Also thiosulfate solutions require frequent standardizations (8, p. 320). In acid solution oxygen of the air will oxidize iodide to iodine.

$$4KI + O_2 + 4HCl \rightarrow 2I_2 + 2H_2O + 4KCl$$
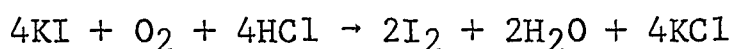
Since many bromination solutions are acidic at least by the time the potassium iodide is added, some precautions must be taken to prevent serious error (8, p. 301).

Direct Methods

Direct methods for the determination of olefinic unsaturation were developed largely to circumvent some of the

disadvantages associated with indirect methods. Direct titrations are more rapid than procedures based on indirect determinations, and the need for determining excess bromine is obviated. Direct methods also avoid the problems associated with relatively long contact times between the unsaturate and excess reagent.

Direct titration methods require that a reliable method be available for determining the end point of the titration. Although visual end points have been used these suffer from the fact that the human eye is not particularly sensitive to the yellow color imparted to the solution by the bromine. Several methods of end point detection have been developed. Many of these are referred to in subsequent paragraphs.

A rapid reaction is essential if a direct titration is to be practical. This is a definite limitation when attempting to apply these techniques. Extensive use has been made of catalysts, generally mercury(II) salts, to accelerate the bromine addition reaction.

Morrell and Levine (22) used naphtha as a solvent for titration of olefins. Bromine in carbon tetrachloride was used as titrant, and the end point was taken as the point where a definite bromine color persisted for thirty seconds.

An equation was used to relate the unknown being determined

to the same known compound titrated under identical condi-

tions.

Stanerson and Levin (29) determined olefins in gaseous

hydrocarbons by titrating with bromine in cold chloroform.

They located the end point by observing a faint color of

bromine persisting for sixty seconds.

Kolthoff and Bovey (16) determined styrene using acidi-

fied methanol-water at $10^{\circ}C$. as solvent and standard bromide-

bromate solution as titrant. The end point was located amper-

ometrically using a rotating platinum electrode.

DuBois and Skoog (9) used standard bromide-bromate solu-

tion as titrant and a mixture of acetic acid, methanol, and

carbon tetrachloride containing some sulfuric acid as solvent.

Simple and branched olefins were titrated using mercury(II)

chloride as catalyst. The end point was determined by an

electrometric method.

Braae (5) also used an electrometric titration for deter-

mination of unsaturation of fast-reacting unsaturates. He

employed a titrant of bromine in carbon tetrachloride which

he standardized iodometrically. His solvent was methanol

made 0.1$\underline{N}$ in hydrobromic acid and 2$\underline{N}$ in hydrochloric acid and

containing 20 grams of mercury(II) chloride per liter.

Sweetser and Bricker (30) employed a spectrophotometric end point for their direct titrations of unsaturated compounds. They used standard bromide-bromate solution as a titrant and a solvent mixture of acetic acid, methanol, and water. They utilized mercury(II) and zinc salts as catalysts.

Leisey and Grutsch (17) determined trace unsaturation in hydrocarbons using coulometrically generated bromine and an amperometric end point. Their solvent was a mixture of acetic acid, methanol, and water containing potassium bromide. They found it necessary to employ a mercury(II) catalyst for the determination of simple and branched olefins.

Miller and DeFord (20) utilized electrically generated bromine and a spectrophotometric end point for the determination of simple and branched olefins. A three to one ratio of acetic acid to methanol containing a small amount of potassium bromide and hydrochloric acid was their solvent. Mercury(II) chloride was used as catalyst.

Williams et al. (33) titrated phenols, unsaturates, and aromatic ethers with standard pyridinium bromide perbromide. For unsaturates they used a solvent of methanol and also found it necessary to employ a mercury(II) chloride catalyst. The end point was determined spectrophotometrically.

SOLVENT CONSIDERATIONS

The choice of solvent can be a very important factor especially when direct titrations are concerned. Solubility properties of all reactants and products must necessarily determine the titration solvent. This means that solvents which are entirely or largely non-aqueous must nearly always be utilized. At the same time it is apparent from observing the mechanism of bromination that the addition of bromine to the double bond should be facilitated by a polar solvent.

The medium employed for bromination undoubtedly plays a major catalytic role. In a nonpolar medium traces of polar compounds can catalyze the bromine addition reaction by causing the reaction to proceed by a polar mechanism rather than a nonpolar free radical reaction. Nozaki and Ogg (23) observed that halide ions catalyzed the addition of halogens to the double bond. Their studies however, failed to show unequivocally the mechanism involved.

Siggia et al. (28) relied primarily on proper choice of solvent to control the reaction of bromine addition at a practical rate for analyzing mixtures of unsaturates by a differential kinetic technique.

Hanna and Siggia (14) studied the relationship between

the rate of addition of bromine to unsaturated compounds and dielectric constant of the solvent. They determined rate constants for various pure solvents and for solvent mixtures of methanol and water. Their data show that as the dielectric constant of the solvent is increased the rate of addition of bromine is accelerated. This is apparently caused by two factors. First, the more polar solvent tends to enhance the separation of charge on the bromine molecule. Second, the initial carbonium ion formed in the first step of the reaction is stabilized by a solvent of high polarity. Hanna and Siggia further state that in solvent mixtures apparently one of the components may locally exert more influence than the other. This causes the solvent effects to be greater than might otherwise be predicted from a consideration only of the over-all dielectric constant of the medium.

Other desirable characteristics which a solvent may possess are cheapness, availability, suitable purity and lack of dangerous properties. While these considerations are secondary, they may warrant some attention if a choice is to be made between two solvents that are otherwise approximately equal.

Catalysts in addition to those discussed above pertaining to solvent properties have been widely used to accelerate the

addition of bromine to the double bond. Hübl (15) used mercury (II) chloride to facilitate addition of iodine to the double bond in the determination of unsaturated carboxylic acids. Since then mercury(II) salts have been a favorite whenever a catalyst has been desired.

EXPERIMENTAL

Direct Titrations

Equipment

All direct titrations were performed using a Beckman Model
B spectrophotometer. The instrument was fitted with a special
titration compartment similar to that used by Fritz and
Pietrzyk (13). A water or air-driven magnetic stirrer obtained
from G. F. Smith Chemical Company and placed directly under the
floor of the compartment was used for stirring the titration
solutions. Two holes drilled in the front wall of the titra-
tion compartment just below the floor accommodated the air or
water hoses. Titration cells were 180 ml. tall-form beakers
with a path length of 4.5 cm. Titrant was delivered from an
ordinary 10 ml. automatic buret which extended through the
cover and dipped into the solution.

Reagents

Approximately 0.12 $\underline{M}$ bromine in glacial acetic acid was
prepared by adding 6.5 ml. of bromine to one liter of glacial
acetic acid. This solution was standardized daily as follows:
To 94 ml. of water in a 180 ml. tall-form beaker 6.0 ml. of
standard 0.1000 $\underline{M}$ arsenious acid (32, p. 356) was added from a
ten ml. buret. This beaker was placed in the special titration
compartment described above and titrated according to the

procedure described below for unsaturated samples.

Solvent systems

All solvents were reagent grade and were used without further purification. The solvent mixtures all reported by volume were all prepared by mixing together the required amounts of the components involved. The total volume at the beginning of the titration was 100 ml. in all cases. It was advantageous to allow solvent mixtures of water and acetic acid to stand for several hours after preparation to rid the solution of air bubbles which form.

A 0.1 $\underline{M}$ mercury(II) chloride solution was prepared by dissolving 27 g. of mercury(II) chloride in one liter of glacial acetic acid. To make the final titration solvent 0.01 $\underline{M}$ in mercury(II) chloride 10 ml. of this solution were substituted for 10 ml. of the glacial acetic acid.

Procedure

To a 180 ml. tall-form beaker containing a Teflon coated stirring bar 85 ml. of glacial acetic acid and 10 ml. of water or 95 ml. of a solvent mixture consisting of 89.5% glacial acetic acid and 10.5% water by volume were added. 5.0 ml. of the sample containing from 0.3 to 1.0 mmole of the compound to be analyzed was pipetted into this solvent mixture and the beaker was placed in the titration compartment of the spectra-

procedure described below for unsaturated samples.

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Procedure

To a 180 ml. tall-form beaker containing a Teflon coated stirring bar 85 ml. of glacial acetic acid and 10 ml. of water or 95 ml. of a solvent mixture consisting of 89.5% glacial acetic acid and 10.5% water by volume were added. 5.0 ml. of the sample containing from 0.3 to 1.0 mmole of the compound to be analyzed was pipetted into this solvent mixture and the beaker was placed in the titration compartment of the spectro-

photometer. The cover was placed on the compartment and the buret tip was extended through the hole and into the titration mixture. The water or air flow through the magnetic stirrer was regulated to give good stirring without the formation of a cone extending down into the solution. The spectrophotometer set at 400 mμ was adjusted to read 0% T (A = ∞) with the shutter closed and 100% T (A = 0.00) with the shutter open. Titrant was then added at a rate of from two to seven ml. per minute until an absorbance of approximately 0.20 was reached. At this point the amount of titrant added and the absorbance reading were recorded. The titration was then continued by adding 0.2 ml. increments of titrant and recording the steady absorbance reading obtained within ten to fifteen seconds after each addition of titrant until an absorbance of approximately 1.5 was reached. This usually gave between four and seven absorbance readings. A plot of absorbance vs. ml. of titrant added was then constructed. The end point was located by the intersection of the straight line drawn through these points with the zero absorbance line. If the compound being titrated tended to react somewhat slowly with bromine it was necessary initially to add the titrant more slowly and to allow a longer period after the addition of each increment of titrant before recording the absorbance.

Indirect Determinations

Equipment

A Bausch and Lomb Spectronic 600 spectrophotometer equip-
ped with a VOM-8 recorder was used for all indirect determina-
tions. A matched set of standard 1x1 cm. quartz cuvettes was
employed as sample cells. A micrometer buret obtained from
Cole Parmer Instrument and Equipment Company was used to
accurately measure and dispense the sample.

Reagents

Approximately 0.12 $\underline{M}$ tribromide in 90% acetic acid-10%
water was prepared by adding 6.5 ml. of bromine to one liter
of a solvent mixture prepared by mixing together 86 ml. of 47%
hydrobromic acid (sp. gr. = 1.49), 32 ml. of water, and 882 ml.
of glacial acetic acid. This gave a solution where the mole
ratio of bromide to bromine was approximately 6:1. For less
concentrated solutions an appropriate amount of this solution
was diluted with the above solvent mixture.

Procedure

2.60 ml. of 0.001 $\underline{M}$ tribromide solution in 90% acetic
acid-10% water was measured accurately into a 1x1 cm. cuvette.
This cuvette was placed in the sample compartment of the
spectrophotometer opposite a matched cuvette containing the
same amount of hydrobromic acid in the same solvent. This

gave an absorbance reading at 410 mμ of approximately 0.5. After this absorbance reading was stable for one minute the cuvette was removed and a 50 to 150 μliter sample containing from 0.2 to 1.6 microequivalents of unsaturate were added. The cuvette was shaken to insure thorough mixing and replaced in the sample compartment. The absorbance was recorded automatically until it remained constant for one minute. The microequivalents of tribromide consumed, which is the same as the microequivalents of unsaturate added, were calculated using Equation 3.

$$\mu\text{eq. of } Br_3^- \text{ consumed} = (M_i)(V_i) - (M_f)(V_f) \tag{3}$$

M_i and M_f are the initial and final tribromide concentrations respectively. These were obtained from a previously prepared plot of absorbance vs. tribromide concentrations. V_i and V_f are the initial and final volumes respectively.

Smaller amounts of unsaturation could be determined by using a more dilute tribromide solution and a lower wavelength where tribromide absorbs more strongly.

Samples

Samples of unsaturates were obtained from several sources including Eastman Organic Chemicals, J. T. Baker Chemical Company, Aldrich Chemical Company, and Mallinkrodt Chemical

Works. All were assumed to be 98 to 100% pure and many were used without further purification. Several of the unsaturated hydrocarbons were purified on a silica gel column (2). Attempts were made to use freshly opened samples in all cases.

The sample solutions were prepared by weighing from three to ten mmoles of unsaturate into a 50 ml. volumetric flask containing some carbon tetrachloride. The contents of the flask was then diluted to the mark with carbon tetrachloride. A 5.0 ml. aliquot was used as sample for the direct titrations. For the indirect determinations a 5.0 ml. aliquot of the first solution was added to a second 50 ml. volumetric flask and diluted to the mark with carbon tetrachloride. Aliquots of this solution were used as samples.

RESULTS AND DISCUSSION

Direct Titrations

Choice of solvent

Several possible solvent systems are available for use in the direct titration with bromine of compounds possessing ethylenic linkages. Acetic acid, because it has found wide use as a solvent for a variety of organic compounds, is a logical choice for use as a solvent for bromination reactions. It is also cheap, readily available in suitable purity so the need for further purification is obviated, has no dangerous properties, and is easy to handle. However, acetic acid has a low dielectric constant ($\varepsilon = 6.15$ at 20°C. for the pure liquid) and as has been discussed above, solvents with a high dielectric constant tend to accelerate the rate of addition of bromine to the double bond. For these reasons it is advantageous to use a mixed solvent system containing approximately 10% water by volume. This amount of water sufficiently accelerates the rate of addition of bromine to the double bond thus making the use of a mercury(II) salt as a catalyst unnecessary in most cases. At the same time the water content of the mixture is low enough to allow complete solubility of all compounds determined and all addition products formed.

The samples were generally dissolved in carbon tetra-
chloride, but any solvent that does not consume bromine or
otherwise adversely affect the titration may be used. Carbon
tetrachloride was used in most cases because it too is a good
solvent for many organic compounds, and it is relatively inert
toward compounds containing a double bond. This apparently is
not true with all solvents. It was observed that low results
were often obtained if the highly reactive olefins such as
cyclohexene were allowed to stand in acetic acid for periods
of one day. These low results may have been caused by the
addition of the components of acetic acid across the double
bond. No such low results were observed when carbon tetra-
chloride was used although nearly all samples were titrated
within a few hours after they were diluted with this solvent.

Glacial acetic acid is used as a solvent for the bromine
titrant. When kept in the reservoir of an automatic buret,
this solution decreases in bromine concentration up to 0.4%
per day. However, if kept in a tightly closed container it
does not decompose appreciably for periods of several weeks.
This indicates that the loss in titer is caused by volatiliza-
tion of the bromine from the solution.

The investigation of other possible suitable solvent

systems was undertaken in an attempt to determine whether a better titration solvent could be found. Because of their high average dielectric constants, mixtures of methanol and water accelerate the addition of bromine to the double bond. However, this acceleration is slight compared to the acetic acid-water system, and erratic results were obtained when these mixtures were used. Although no definite conclusions could be made regarding these observations, presumably these results were caused by limited solubility of various unsaturates in the mixtures. Also impurities present in the methanol or arising from another source could have reacted with the bromine and contributed to the erratic results obtained. For these reasons methanol-water mixtures were not used as titration solvents.

Attempts were made to substitute formic acid for acetic acid and methanol for water in the acetic acid-water solvent. No particular advantage could be observed in either case, and in the latter case the rate of bromine addition was markedly slowed.

End point detection

The human eye is relatively insensitive to the yellow color imparted to the titration solution by excess elemental bromine. Consequently accurate visual location of the end

point of a titration is quite difficult, and some other method of locating the end point is desirable.

Because of the color of the titrant itself, spectrophotometric end points are particularly adaptable to titrations with standard solutions of bromine. Miller and DeFord (20) point out some of the advantages of using this technique for titrations with bromine. The sensitivity of the end point can be varied by changing the wavelength setting because the extinction coefficient of bromine is dependent upon wavelength. Also the difficulty of accurately locating end points for reactions which are slow in the vicinity of the end point is lessened because linear portions of the titration curve before and after the end point are extrapolated.

Figure 1 shows spectrophotometric titration curves for the titration of cyclohexene and of allyl ether with 0.12 $\underline{M}$ bromine in glacial acetic acid. These curves for cyclohexene and allyl ether are typical of those obtained for compounds which add bromine rapidly and somewhat more slowly, respectively.

Titrations without mercury(II) catalyst

Table 1 shows the results of direct titrations of various unsaturated compounds with 0.12 $\underline{M}$ bromine in glacial acetic acid in 85% acetic acid-10% water-5% carbon tetrachloride.
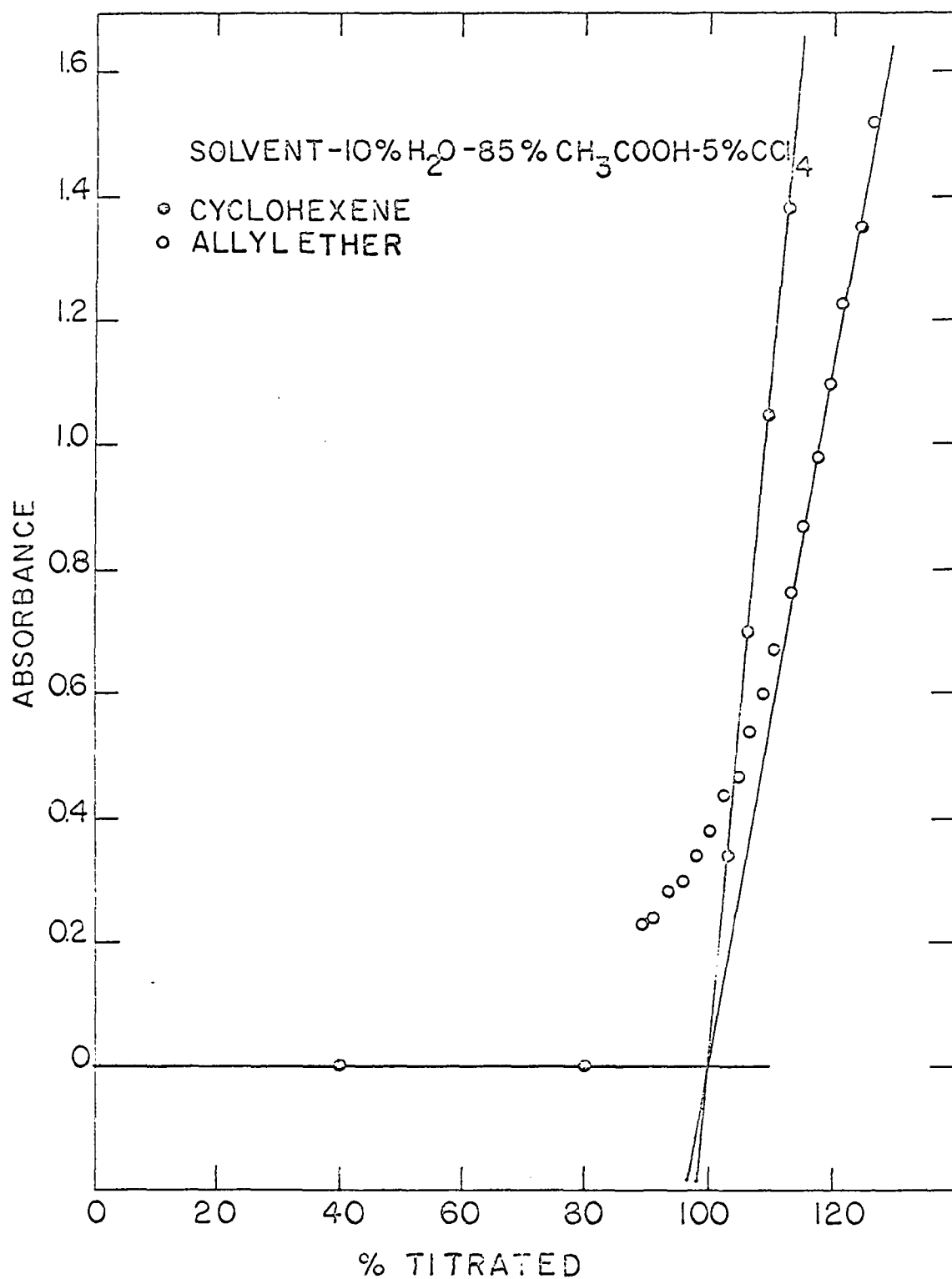
Fig. 1. Spectrophotometric titration curves for cyclohexene and allyl ether with 0.12 $\underline{M}$ bromine in glacial acetic acid

Table 1. Direct titrations with 0.12 $\underline{M}$ bromine in glacial acetic acid in 85% acetic acid-10% water-5% carbon tetrachloride

Compound[a]	% Found[b]	Number of determinations
Allyl acetate	Reacts slowly[c]	-
Allyl alcohol	96.0 ± 0.3%	4
Allyl ether	93.9 ± 0.8%[d,e]	2
3-Bromopropene	Does not react[f]	-
3-Butenenitrile	Does not react[f]	-
3-Butyn-1-ol	Does not react[f]	-
trans-Cinnamaldehyde	Does not react[f]	-
trans-Cinnamic acid	Does not react[f]	-
Cyclohexene	100.0 ± 0.4%	4
Cyclohexylacetylene	0.2 ± 0.1%	4
2,3-Dimethyl-2-butene	100.0 ± 0.2%	2
2,5-Dimethyl-2-hexene	98.6 ± 0.4%	2
trans-2,5-Dimethyl-3-hexene	110.3 ± 0.0%	2
Ethyl acrylate	Does not react[f]	-
3-Ethyl-2-pentene	113.8 ± 0.5%	4
Ethynylbenzene	Reacts slowly[c]	-
trans-3-Hexene	99.8 ± 0.2%	4
Isoprene	100.6 ± 0.1%[g]	4

[a]Amounts taken range from 0.3 to 1.0 mmole.

[b]Results based on assuming that samples are 100% pure.

[c]Reacts too slowly to be determined.

[d]Results based on the assumption that both double bonds add bromine.

[e]Twenty to twenty-five minutes required per determination.

[f]No detectable reaction in five minutes.

[g]Results based on the assumption that only one double bond adds bromine.

Table 1. (Continued)

Compound[a]	% Found[b]	Number of determinations
d-Limonene	99.2 ± 0.5%[d]	2
1-,2-Octene	100.4 ± 0.3%	4
1,4-Octadiene	Interferes[h]	-
Oleic acid	97.2 ± 0.5%	4
1,3-Pentadiene	99.6 ± 0.4%[g]	2
Pyrrole	Interferes[h]	-
Styrene	100.0 ± 0.1%	4

[h]Initial rapid reaction followed by much slower reaction. No end-point observed.

All results are calculated assuming that all compounds are 100% pure. Amounts taken range from 0.3 to 1.0 mmole in each case. Cyclohexene, trans-3-hexene, isoprene, d-limonene, and 1-,2-octene (mixture of isomers) were all purified on a silica gel column before determination. All other compounds were used as received except allyl alcohol which was purified by fractional distillation.

Good results were obtained for cyclohexene; 2,3-dimethyl-2-butene; 2,5-dimethyl-2-hexene; trans-3-hexene; isoprene; d-limonene; 1-,2-octene (mixture of isomers); oleic acid; 1,3-pentadiene; and styrene. All of these compounds react rapidly with bromine and the titrations proceed very smoothly.

Table 1.   (Continued)

Compound[a]	% Found[b]	Number of determinations
d-Limonene	99.2 ± 0.5%[d]	2
1-,2-Octene	100.4 ± 0.3%	4
1,4-Octadiene	Interferes[h]	-
Oleic acid	97.2 ± 0.5%	4
1,3-Pentadiene	99.6 ± 0.4%[g]	2
Pyrrole	Interferes[h]	-
Styrene	100.0 ± 0.1%	4

[h]Initial rapid reaction followed by much slower reaction. No end-point observed.

All results are calculated assuming that all compounds are 100% pure. Amounts taken range from 0.3 to 1.0 mmole in each case. Cyclohexene, trans-3-hexene, isoprene, d-limonene, and 1-,2-octene (mixture of isomers) were all purified on a silica gel column before determination. All other compounds were used as received except allyl alcohol which was purified by fractional distillation.

Good results were obtained for cyclohexene; 2,3-dimethyl-2-butene; 2,5-dimethyl-2-hexene; trans-3-hexene; isoprene; d-limonene; 1-,2-octene (mixture of isomers); oleic acid; 1,3-pentadiene; and styrene. All of these compounds react rapidly with bromine and the titrations proceed very smoothly.

A typical titration for determination of one of these compounds can be completed in two to three minutes or less.

The results for isoprene and 1,3-pentadiene, which both contain two conjugated double bonds, are calculated assuming that one mole of bromine will react with one mole of each compound. In these cases it is necessary to complete the titrations as rapidly as possible to reduce the possibility of a second mole of bromine beginning to add to the compound.

d-Limonene which contains two isolated double bonds readily adds two moles of bromine, and the results for this compound are calculated on this basis. Bromine consumption does not appear to become slower after sufficient bromine has been added to quantitatively brominate only one double bond per molecule. This observation leads to the conclusion that the two double bonds react independently.

A titration of oleic acid using coulometrically generated tetrabutylammonium hydroxide gives a value of 98.3% which compares favorably with the results given in Table 1.

Allyl acetate, allyl alcohol, and allyl ether all react more slowly than compounds possessing simple olefinic linkages. As Table 1 shows, allyl acetate reacts too slowly to be determined by direct titration with bromine. Allyl ether, which

contains two isolated double bonds like d-limonene, adds two moles of bromine. This compound also reacts quite slowly and requires from 20 to 25 minutes per determination. Allyl alcohol reacts most rapidly of the three and can be determined with good precision. The low results obtained for the latter two compounds quite possibly are caused by the slowness of the addition of bromine, although the source of error could be the presence of an impurity containing no reactive unsaturation. The slowness of the addition reaction for these three compounds is attributed to the electron-withdrawing effects of the various oxygen atoms allylic to the double bond.

The compounds 3-bromopropene, 3-butenenitrile, 3-butyn-1-ol, trans-cinnamaldehyde, trans-cinnamic acid, and ethyl acrylate do not react in the short time required for the completion of a direct titration of those compounds that readily add bromine to the double bond. Cyclohexylacetylene may also be included in this group if the very small blank obtained with this compound is attributed to an olefinic impurity. The allylic nitrile group and the allylic bromine are both strong electron-withdrawing substituents and deactivate the double bond. trans-Cinnamic acid, trans-cinnamaldehyde, and ethyl acrylate which have a double bond conjugated with a carbonyl

group also fail to add bromine. Cyclohexylacetylene and 3-butyn-1-ol fail to react, but ethynylbenzene reacts slowly. This reaction is rapid enough to interfere with the direct titration of a fast reacting compound, but much too slow for determination of the ethynylbenzene by direct titration.

1,4-Octadiene rapidly consumes bromine up to a point where approximately one mole of bromine has been added per mole of 1,4-octadiene present. The reaction then slows markedly, but further consumption of bromine continues. This slower addition reaction is sufficiently slow to preclude a direct titration, but is rapid enough to prevent even rough estimation of the location of the end point.

Pyrrole also consumes bromine, but again no end point can be located even after the mole ratio of bromine added to pyrrole present is greater than 3:1. A green color is formed that effectively obscures the yellow color which excess bromine imparts to the solution. Although this compound can not be determined, it will definitely interfere with attempts to determine other unsaturated compounds in its presence.

High results are obtained for trans-2,5-dimethyl-3-hexene and 3-ethyl-2-pentene. Compounds of this type typically give high results presumably because of substitution which takes

place along with addition. Attempts were made to reduce this substitution error by modifying titration conditions. The use of a solvent of 95% acetic acid-5% carbon tetrachloride gave results which were approximately 6% low for 3-ethyl-2-pentene and 1.5% high for trans-2,5-dimethyl-3-hexene. When the acetic acid-water-carbon tetrachloride solvent was cooled in an ice bath for 30 minutes before the titration was begun, the results obtained for 3-ethyl-2-pentene were approximately 7% high. Using tribromide ion in acetic acid as titrant and 0.11 $\underline{M}$ hydrobromic acid in 85% acetic acid-10% water-5% carbon tetrachloride as solvent gave results which were 8% high for the hexene compound and 13% high for the pentene compound. It was also noted in all cases that after the titration was completed the yellow color imparted to the solution by the excess bromine present gradually disappeared indicating that a slow bromine consuming reaction was occurring. This reaction presumably consisted of substitution of bromine for hydrogen.

Because of the possibility that impurities could be present, the purities of the 3-ethyl-2-pentene and trans-2,5 dimethyl-3-hexene were ascertained by gas chromatography. Both compounds when analyzed using a 20' x ¼" o.d., 10% SE52 on 100/120 mesh DMCS treated Chromosorb W were shown to be

99+% pure. A flame ionization detector at 150°C. with the column at 70°C. and the inlet at 100°C. was used. The flow rate was 100 ml./min.

All of these observations are concordant with the view that the addition reaction is accompanied by a relatively slow but significant substitution reaction for these compounds.

In an effort to check the method under investigation the 3-ethyl-2-pentene and trans-2,5-dimethyl-3-hexene were analyzed by two other methods. ASTM standard color-indicator method D1158 (3), an indirect procedure with a 40 second reaction time gave results which were 24% high for 3-ethyl-2-pentene and 17% high for trans-2,5-dimethyl-3-hexene. This method utilizes a solvent system of acetic acid and carbon tetrachloride. The bromine is liberated from a standard bromide-bromate solution and the excess is determined by an indirect iodometric method.

The substitution method of Polgár and Jungnickel (24, p. 237) which is especially designed to correct for any substitution which takes place gave results which were 4% and 6% high respectively for the pentene and the hexene compounds.

Unger (31) studied the influence of structure on the determination of several olefins by various bromination

methods. He was able to obtain good results for branched olefins by using a solvent system of acetic acid-methanol-carbon tetrachloride acidified with sulfuric acid although simple olefins generally gave low results. He also obtained high results in most cases when following standard ASTM procedures.

Titration of mixtures

Examination of the data shown in Table 1 reveals the possibility that the determination of those compounds which readily add bromine may be accomplished in the presence of and without interference from the unreactive compounds. The results for the analysis of the reactive components of several mixtures are given in Table 2. Using the results given in Table 1 as a guide, other similar mixtures could be analyzed with analogous results. The data contained in Table 2 are for only a representative sample of the possible mixtures for which quantitative results could be obtained.

As has been noted above, allyl alcohol adds bromine somewhat slowly. Therefore, the slightly higher results obtained for this compound when titrated in the presence of trans-cinnamic acid than when titrated alone may be caused by the trans-cinnamic acid beginning to add bromine. Another possibility is that some bromine consuming impurity is present in

Table 2. Direct titrations of mixtures with bromine in glacial acetic acid in 85% acetic acid-10% water-5% carbon tetrachloride

Compound[a] titrated	Other compound[b] present	% Found[c]	Number of determinations
Allyl alcohol	None	96.0 ± 0.3%	4
Allyl alcohol	trans-Cinnamic acid	97.3 ± 0.6%	4
Cyclohexene	None	100.0 ± 0.4%	4
Cyclohexene	3-Butenenitrile	100.1 ± 0.1%	4
trans-3-Hexene	None	99.8 ± 0.2%	4
trans-3-Hexene	Cyclohexylacetylene	100.4 ± 0.2%	4
1-,2-Octene	None	100.4 ± 0.3%	4
1-,2-Octene	trans-Cinnamaldehyde	100.6 ± 0.2%	4
1,3-Pentadiene	None	99.0 ± 0.2%	4
1,3-Pentadiene	trans-Cinnamaldehyde	99.8 ± 0.2%	4

[a]Amounts taken range from 0.4 to 1.1 mmoles.

[b]Equimolar amounts of other compound taken.

[c]Results based on the assumption that all samples are 100% pure.

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the _trans_-cinnamic acid, although as Table 1 shows none was detected when this compound was titrated alone.

The results for the determination of cyclohexene in the presence and the absence of 3-butenenitrile agree very closely and are within experimental error.

trans-3-Hexene gives slightly higher results when titrated in the presence of cyclohexylacetylene than when titrated alone. However, subtraction of the value obtained for the cyclohexylacetylene blank shown in Table 1 brings the two results into close agreement.

Slightly higher results are obtained for 1-,2-octene when determined alone than when determined in the presence of _trans_-cinnamaldehyde, although the two results agree within experimental error.

Analysis of 1,3-pentadiene in the absence and presence of _trans_-cinnamaldehyde gives slightly higher results in the latter case.

Titrations with mercury(II) catalyst

Table 3 shows the results obtained for titration of several compounds with 0.12 $\underline{M}$ bromine in glacial acetic acid in 85% acetic acid-10% water-5% carbon tetrachloride employing 0.01 $\underline{M}$ mercury(II) chloride as a catalyst. The use of a

mercury(II) salt to facilitate the addition of bromine to the double bond has been discussed above.

Table 3. Direct titrations with 0.12 $\underline{M}$ bromine in glacial acetic acid in 85% acetic acid-10% water-5% carbon tetrachloride using 0.01 $\underline{M}$ mercury(II) chloride as a catalyst

Compound[a]	% Found[b]	Number of determinations
Allyl acetate	98.1 ± 1.8%	4
Allyl ether	99.7 ± 0.6%[c]	4
3-Bromopropene	96.2 ± 0.0%	2
3-Butenenitrile	Reacts slowly[d]	-
trans-Cinnamaldehyde	Reacts slowly[d]	-
trans-Cinnamic acid	Reacts slowly[d]	-
Cyclohexylacetylene	Reacts slowly[d]	-
Ethyl acrylate	Reacts slowly[d]	-
Isoprene	134.7 ± 2.9%[e]	2
1,4-Octadiene	96.1 ± 0.0%[c]	4

[a]Amounts taken range from 0.3 to 1.0 mmoles.

[b]Results based on the assumption that samples are 100% pure.

[c]Results based on the assumption that both double bonds add bromine.

[d]Reacts too slowly to make a direct titration practical.

[e]Results based on the assumption that only one double bond adds bromine.

Inspection of Table 3 shows that the utilization of a mercury(II) chloride catalyst allows the determination of allyl acetate, 3-bromopropene, and 1,4-octadiene by direct titration. These results can be compared to those shown in Table 1 for the same compounds titrated in the absence of mercury(II) catalyst.

The use of mercury(II) chloride allows better results to be obtained for the direct titration of allyl ether. The improvement of the results for this compound, which is assumed to add two moles of bromine per mole of ether, is probably due to the increased rate of addition of bromine. The use of the mercury(II) chloride makes a complete titration possible in two or three minutes.

3-Butenenitrile, trans-cinnamaldehyde, trans-cinnamic acid, cyclohexylacetylene, and ethyl acrylate all add bromine slowly in the presence of mercury(II) chloride. The compounds react too slowly to make a direct titration practical, but they do react rapidly enough to preclude precise or accurate location of the end point when attempting to determine one of the faster-reacting compounds in their presence. The use of a mercury(II) chloride catalyst then causes a loss of selectivity and eliminates the possibility of determining compounds with

reactive olefinic unsaturation in the presence of those that are less reactive.

The direct titration of isoprene in the presence of the mercury(II) catalyst leads to high results for this compound. Apparently the catalyst increases the reactivity enough to promote addition of a second mole of bromine to the compound. This reaction is rapid enough to prevent location of the end point. However, this second mole does not add rapidly enough to permit a practical direct titration involving the addition of two moles of bromine to each mole of isoprene present.

Point-slope end point location

One disadvantage of using a spectrophotometric end point is the necessity of recording and plotting several absorbance readings obtained as increments of titrant are added. This technique is especially inconvenient if routine analysis of a large number of similar compounds is involved.

If the slope of the upper portion of the titration curve past the end point (refer to Figure 1) is accurately known, any one point on this part of the curve will permit determination of the point where this portion of the curve intersects the zero absorbance line. The end point for the titration is then accurately located. If the slope of the upper portion of the

curve remains constant from one titration to another, precise location of the end point is possible provided conditions do not vary appreciably from one titration to another.

Examination of Figure 2 and Figure 3 reveals that to standardize conditions it is necessary to employ a solvent which contains sufficient hydrobromic acid to insure that the molar ratio of bromide ion to bromine is not less than 6:1 at any time during the titration. For this reason the titration solvent is made 0.011 M in hydrobromic acid when this technique for end point location is used. Otherwise conditions for these titrations are identical to those used for the direct titrations described above.

To obtain the slope of the upper portion of the titration curve a sample of cyclohexene was titrated in the solvent containing hydrobromic acid according to the standard direct titration procedure. The slope of the upper portion of the titration curve was found to be 4.7.

Table 4 shows results obtained for the direct titration of three different compounds using this point-slope technique for end point location. These results compare very favorably with the results given in Table 1 for the same compounds and demonstrate the feasibility of using this technique.

Table 4. Direct titrations in 0.011 M hydrobromic acid in
85% acetic acid-10% water-5% carbon tetrachloride
with 0.12 M bromine in glacial acetic acid

Compound[a]	% Found[b]	Number of determinations
Cyclohexene	100.0 ± 0.2%	4
trans-3-Hexene	99.6 ± 0.6%	4
1-,2-Octene	99.6 ± 0.4%	4

[a]Amounts taken range from 0.2 to 0.8 mmoles.

[b]Results based on the assumption that samples are 100% pure.

Interferences

Table 5 shows the results of a study undertaken to determine the feasibility of utilizing various solvent systems of the type 85% acetic acid-10% water-5% other compound for determination of olefinic unsaturation by direct titration with bromine in glacial acetic acid. Blank titrations were run using these various solvent systems under conditions which approximated as nearly as possible those existing during the direct titration of an unsaturate which readily adds bromine. The stability of the yellow color imparted to the solution by the bromine was observed visually after the termination of all blank determinations. If the color gradually disappeared, the time for total bromine consumption was noted.

Table 5. Blank titrations of various solvent mixtures consist-
          ing of 85% acetic acid-10% water-5% other compound
          with 0.12 M bromine in glacial acetic acid

Other compound	Interference	Comments
Acetic anhydride	None	-
Acetone	None	Solution completely de-colorizes in one hour
Carbon disulfide	None	-
Cyclohexylamine	None	Small blank
N,N-Dimethylformamide	None	-
Dimethyl sulfoxide	None	-
Isovaleraldehyde	None	Solution completely de-colorizes in 10 minutes
Pyridine	None	Small blank

None of the compounds listed in Table 5 consume bromine
during the short time required for a direct titration to be
performed. The solvent mixtures containing isovaleraldehyde
and acetone become completely decolorized in ten minutes and
one hour respectively, indicating that these compounds react
slowly with bromine.

A small blank for which a correction can be applied is
observed for the solvent mixtures containing cyclohexylamine
and pyridine. This blank is presumably due to some impurity
in these compounds present in small amounts.

The results of this study indicate that any of the com-
pounds listed in Table 5 may be substituted for the carbon

tetrachloride portion of the solvent mixture used for the determinations reported in Tables 1 and 2.

The results of blank titrations of several solvent mixtures consisting of 0.01 $\underline{M}$ mercury(II) chloride is 85% acetic acid-10% water-5% other compound are shown in Table 6. These results can be compared with those shown in Table 5 for the same solvents in the absence of the mercury(II) catalyst. Again the titration conditions approximate the conditions present during direct titration of a fast-reacting unsaturate.

Table 6. Blank titrations of various solvent mixtures consisting of 0.01 $\underline{M}$ mercury(II) chloride in 85% acetic acid-10% water-5% other compound with 0.12 $\underline{M}$ bromine in glacial acetic acid

Other compound	Interference	Comments
Acetic anhydride	None	-
Acetone	None	Solution completely decolorizes in 45 minutes
Carbon disulfide	None	-
Cyclohexylamine	Interferes	Cloudy solution forms
N,N-Dimethylformamide	None	-
Dimethyl sulfoxide	Interferes	Readily consumes bromine
Isovaleraldehyde	None	Solution completely decolorizes in one minute
Pyridine	Interferes	Readily consumes bromine

No difference in the behavior of acetic anhydride, carbon disulfide, and N,N-dimethylformamide is observed. These three compounds apparently do not consume bromine either in the

absence or the presence of the mercury(II) chloride.

Solutions containing 5% isovaleraldehyde are completely discolorized within one minute when the solution is 0.01 $\underline{M}$ in mercury(II) chloride. This is compared to nearly ten minutes required for complete disappearance of the bromine color when no mercury(II) chloride is added to the solvent. Acetone likewise is more prone to react with bromine when the solution contains mercury(II) chloride. The times required for complete decolorization in these cases are one hour for the solution without and 45 minutes for the solution with the mercury(II) salt.

Cyclohexylamine, dimethyl sulfoxide, and pyridine in contrast to their behavior in solutions containing no mercury(II) chloride can not be tolerated in amounts of 5% in solutions made 0.01 $\underline{M}$ in mercury(II) chloride. Cyclohexylamine forms a cloudy solution which precludes the use of a titration employing a spectrophotometric end point. Dimethyl sulfoxide and pyridine both readily consume bromine thus rendering these solvents unsuitable for use in these instances.

Table 7 lists some non-olefinic compounds which consume bromine when present in amounts of from 0.5 to 0.7 mmole in the titration solvent used for the direct titration of compounds possessing olefinic unsaturation. As would be expected

compounds containing sulfur not in its highest oxidation state consume bromine.

Table 7. List of non-olefinic compounds which consume 0.12 $\underline{M}$ bromine in glacial acetic acid when present in 85% acetic acid-10% water-5% carbon tetrachloride[a]

Ethyl disulfide	n-Propyl sulfide[b]
1-Hexanethiol	Aniline
Phenol	

[a]Amounts taken range from 0.5 to 0.7 mmole.

[b]Can be determined quantitatively by direct titration.

1-Hexanethiol initially consumes bromine rapidly. As more bromine is added consumption proceeds at a slower rate which is still too rapid to permit observation of any end point. Addition of bromine was continued until the mole ratio of bromine added to mercaptan present was approximately 2.8:1. Gradual disappearance of the bromine was still occurring at this point.

Ethyl disulfide also consumes bromine but at a relatively slow rate. Again no end point could be detected and the titration was discontinued at a point where the molar ratio of bromine to disulfide was approximately 3:2.

n-Propyl sulfide consumes bromine at a rate comparable to that of a fast-reacting unsaturate and gives a clear, sharp

end point. This compound, while it would definitely interfere
with a titration of olefinic unsaturation, can be determined
quantitatively using the same procedure as that used for direct
titration of unsaturated compounds. Siggia (27, p. 138) has
developed a similar procedure for direct titration of dialkyl
sulfides. He used standard bromide-bromate solution as
titrant and located the end point visually.

Siggia (27, p. 162) described an indirect method for the
determination of phenol and aniline which is based on the
substitution of bromine for hydrogen in the ortho and para
positions of these compounds. Three moles of bromine are con-
sumed per mole of phenol or aniline present. Therefore, these
compounds can be expected to consume bromine and to thereby
interfere with the direct titration of compounds containing
olefinic unsaturation. It is observed that both compounds
initially react rapidly with bromine. However, as the titra-
tion is continued the reaction becomes considerably slower
although not slow enough to permit location of an end point.
The titrations were discontinued when the mole ratios of
bromine to phenol and bromine to aniline were approximately
1.3:1 and 2.7:1 respectively.

Role of mercury(II) catalyst

A good case can be made against indiscriminate use of a mercury(II) salt to accelerate the rate of addition of bromine to the double bond. Wood (34) omitted the mercury(II) chloride catalyst from the procedure described by DuBois and Skoog (9). The method which he called the modified electrometric method is a direct titration procedure utilizing an electrometric end point and standard bromide-bromate as titrant. Results for the determination of propylene and butylene polymers were significantly improved when the mercury(II) catalyst was not employed.

Unger (31) analyzed 45 straight chain and branched olefins by several methods and also found that in general the omission of catalyst improved results.

As has been pointed out above the rate of addition of bromine to compounds which are ordinarily relatively unreactive toward the addition of bromine is accelerated by a mercury(II) catalyst. This means that these slow reacting compounds will interfere with the determination of fast-reacting unsaturates if a mercury(II) salt is present. The catalyst therefore tends to destroy any selectivity based on the relative reactivities of bromine with various unsaturated compounds.

Another somewhat more subtle reason for performing

bromine addition reactions in the absence of a mercury(II) catalyst is revealed by observing the behavior of bromine toward 3-bromopropene in the absence and presence of catalyst as shown in Table 1 and Table 2 respectively. In the absence of mercury(II) chloride the compound fails to react in the time normally required for direct titration of a fast-reacting olefin, but in the presence of the salt bromine adds to the double bond, and nearly quantitative results can be obtained. 3-Bromopropene possesses a bromine atom allylic to the double bond. An analogous situation exists if substitution of bromine for hydrogen takes place at the highly reactive allylic position of a normal unsaturated compound. The results obtained for 3-bromopropene therefore indicate that if such substitution does take place further addition is unlikely to occur in the absence of catalyst but is likely to occur in the presence of catalyst. In other words if mercury(II) chloride is not present addition and substitution are mutually exclusive provided the substitution occurs first, but if mercury(II) chloride is present both reactions may occur. In the former case only one mole of bromine will be consumed per mole of unsaturate, and the analytical result will be identical regardless of which occurs. In the latter case two moles of bromine will be consumed per mole of unsaturate and high results will be

obtained.

Also, as can be seen from examination of Tables 5 and 6, the number of non-olefinic interferences is significantly increased in the solutions containing mercury(II) chloride as catalyst.

Indirect Determinations

The determination of small amounts of olefinic unsaturation can be accomplished by using an indirect spectrophotometric method. The brominating species used in this procedure is the tribromide ion. The method is based on the decrease in absorbance resulting from consumption of the tribromide ion by reaction with an unsaturate. Because a small total volume of solution is used, a small consumption of tribromide ion causes a proportionately large change in the concentration of this species. This change in tribromide ion concentration is measured spectrophotometrically by employing a Beer's law plot of tribromide ion concentration vs. absorbance. The amount of unsaturate present is calculated assuming that one mole of tribromide ion will react with one mole of a compound containing one double bond.

Choice of solvent

The original intent was to use bromine in 90% acetic acid-

10% water as the brominating species for the indirect deter-
minations of olefinic unsaturation. However, attempts to use
this system always gave results which were from 20 to 40% low.
Because the occurrence of sufficient evaporation of the unsat-
urates seemed unlikely to cause such low results, and because
quantitative results were obtained for these same unsaturates
when determined by direct titration, it was necessary to
investigate the problem further. Since the whole procedure
was based on the measurement of the absorbance of the bromine
solution before and after the bromination reaction, a likely
place for complications was in this area. If some species
produced during the course of the reaction between bromine
and the unsaturated compound absorbed more strongly than the
bromine which had originally been present and subsequently
consumed by the unsaturate, the resulting decrease in absorb-
ance caused by the consumption of bromine would be too small.
This would cause the illusion that less bromine had been con-
sumed than was actually the case.

Figure 2 shows the effect of various amounts of hydro-
bromic acid on the absorption of bromine in 90% acetic acid-
10% water. It is obvious from the absorption curves shown in
this figure that a small amount of hydrobromic acid signifi-
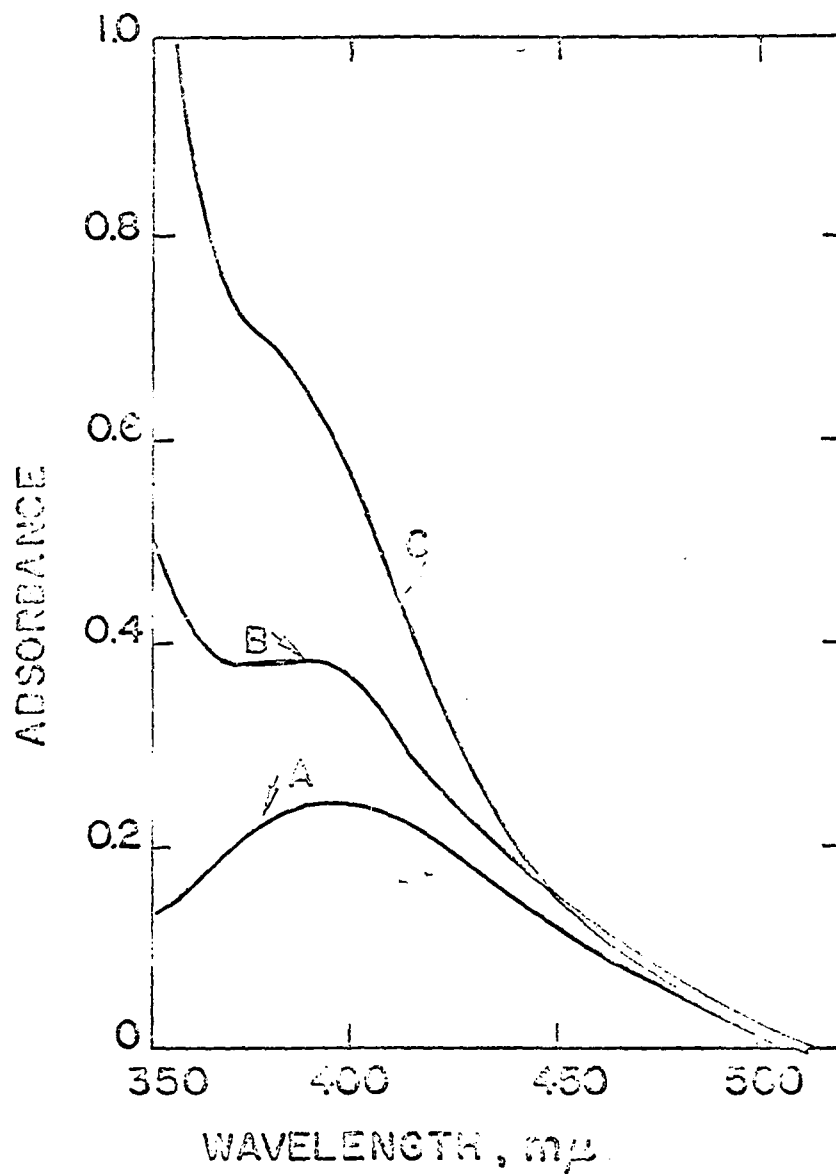cantly increases the absorbance at 410 mμ. From these

Fig. 2. Absorption spectra of 0.00146 $\underline{M}$ Br$_2$ in 90% acetic
acid-10% water in the presence of various amounts
of hydrogen bromide
A. Br$_2$ with no HBr added
B. Molar ratio of HBr to Br$_2$ is approximately 1:1
C. Molar ratio of HBr to Br$_2$ is approximately 6:1

observations it was concluded that hydrobromic acid produced during the course of the addition reaction was combining with the unconsumed bromine to produce the tribromide ion. This species, because it absorbed more strongly than bromine itself, caused a higher absorbance than should have been observed.

Figure 3 shows a plot of absorbance vs. the mole ratio of hydrobromic acid to bromine. It can be seen from this plot that at mole ratios of 6:1 or greater the absorbance remains constant. Therefore, if the original reaction medium contains hydrobromic acid and bromine in a 6:1 molar ratio, any further increase in hydrobromic acid concentration will not affect the absorbance. When this solvent system was utilized in the indirect determination, the results obtained were immediately improved.

Experimental results

Typical titration curves for the determination of cyclo-hexene which readily adds bromine and for allyl ether which reacts more slowly are shown in Figure 4. The absorbance is allowed to become stable for one minute, then the lid to the sample compartment is opened, sample is added, and the cuvette is shaken to thoroughly mix the contents. The discontinuity in the curve is caused by this opening of the lid of the sample compartment. The cuvette is replaced and the reaction is
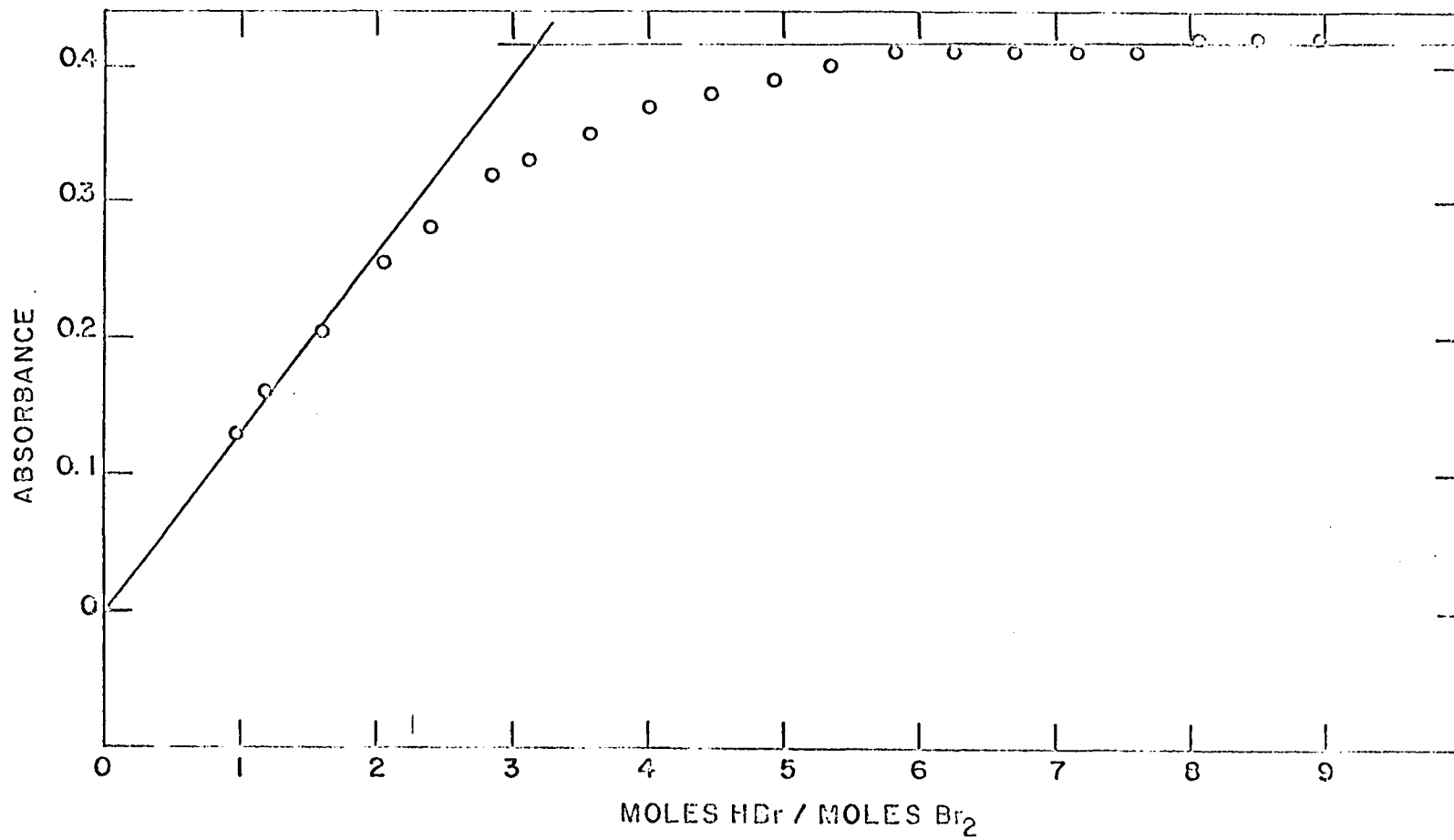
Fig. 3. Effect of hydrogen bromide on the absorbance of bromine in 90% acetic acid-10% water at 410 mμ
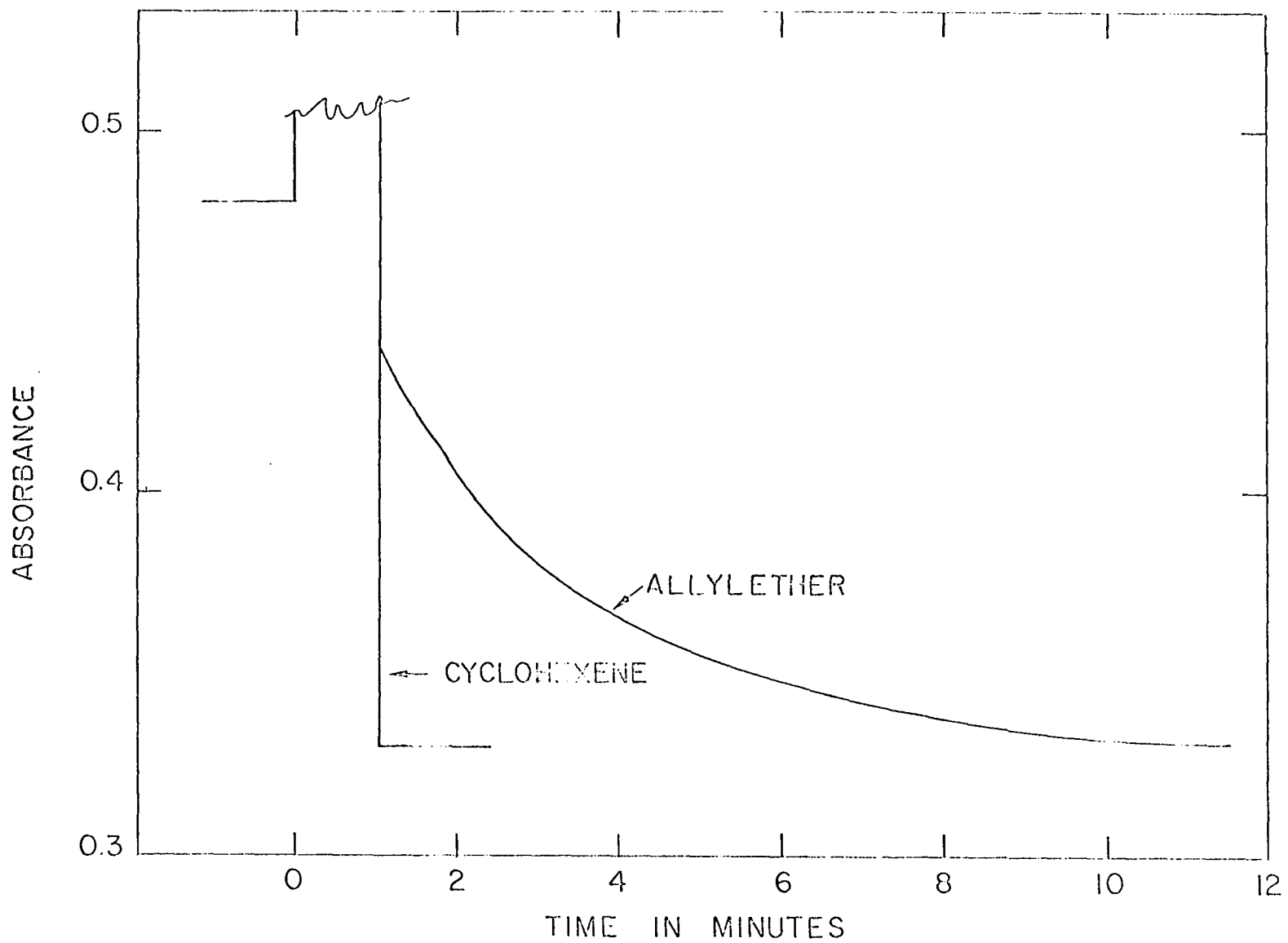
Fig. 4. Curves for the indirect determination of cyclohexene and allyl ether

allowed to continue until the absorbance is again constant for one minute.

The results of several indirect determinations in a solvent consisting of 90% acetic acid and 10% water by volume are shown in Table 8. Amounts of unsaturate taken in all cases range from 0.3 to 1.1 μmoles and all results are based on the assumption that samples are 100% pure.

The results for allyl alcohol tend to be slightly more than 2% lower than is found for this compound using the direct titration method. It was observed however that lower results were obtained for allyl alcohol when determined by direct titration when the solution was made 0.002 $\underline{M}$ in hydrobromic acid prior to the beginning of the titration. It is possible that the tribromide ion is not as effective for the addition of bromine to allyl alcohol or that the alcohol is partially converted to the corresponding bromide thus rendering it inactive toward the addition of bromine.

Allyl ether adds bromine quite slowly. This fact probably accounts for the slightly low results obtained for this compound. Both double bonds of allyl ether add bromine and no observations were made to indicate that the two double bonds do not react independently.

trans-Cinnamaldehyde and ethyl acrylate show no detect-

Table 8.   Indirect determinations in 90% acetic acid-10% water

Compound[a]	Results[b]	Number of determinations
Allyl alcohol in CCl_4	93.7 ± 3.0%	14
Allyl ether in CCl_4	94.9 ± 3.1%[c]	7
trans-Cinnamaldehyde in CCl_4	Does not react[d]	-
Cyclohexene in benzene	97.8 ± 6.0%	9
Cyclohexene in CCl_4	99.0 ± 2.0%	8
Cyclohexene in CCl_4[e]	100.9 ± 0.5%	3
Cyclohexene in methanol	100.4 ± 0.6%	3
2,3-Dimethyl-2-butene in CCl_4	96.6 ± 4.0%	7
trans-2,5-Dimethyl-3-hexene in CCl_4	101.8 ± 3.9%	3
Ethyl acrylate in CCl_4	Does not react[d]	-
3-Ethyl-2-pentene in CCl_4	99.7 ± 5.0%	3
Isoprene in CCl_4	101.2 ± 1.5%[f]	4
d-Limonene in CCl_4	96.3 ± 5.3%[c]	9
1-,2-Octene in CCl_4	96.0 ± 1.1%	3
1-,2-Octene in methanol	97.0 ± 4.5	5

[a]Amounts taken range from 0.3 to 1.1 μmoles.

[b]Results based on the assumption that samples are 100% pure.

[c]Results based on the assumption that both double bonds add bromine.

[d]No detectable reaction in ten minutes.

[e]Equimolar amount of allyl acetate present.

[f]Results based on the assumption that only one double bond adds bromine.

able reaction in ten minutes. Hence, it would be possible to determine a compound reacting in this time or less in the presence of these compounds. Compounds which behave similarly to trans-cinnamaldehyde and ethyl acrylate toward bromine addition would be expected to react in an analogous manner.

Within experimental error cyclohexene in benzene, carbon tetrachloride, and methanol give quantitative results in all cases. It is also possible to determine quantitatively cyclohexene in the presence of an equimolar amount of allyl acetate.

2,3-Dimethyl-2-butene in carbon tetrachloride gives slightly low but nearly quantitative results.

trans-2,5-Dimethyl-3-hexene and 3-ethyl-2-pentene give good results which can be contrasted to the high results obtained for these compounds when determined by direct titration. As discussed above these high results are attributed to a bromine consuming side reaction and are obtained even when titration conditions are modified. During the indirect determination the final absorbance remains constant for five minutes or longer indicating that no slow substitution reaction is occurring. A possible explanation for the discrepancy between the results obtained from the two methods is as

follows: Excess bromine enhances the possibility of a sub-
stitution reaction, especially for reactive compounds of the
type under discussion.   Although excess bromine is present
during the indirect method, a higher concentration of bromine
is present during direct titration where the titrant stream
enters the titration solution.   Hence, for these compounds
substitution may occur to a larger extent during the direct
titration procedure.

Results for isoprene, calculated on the basis that only
one mole of bromine reacts with one mole of isoprene, tend to
be slightly high.   This very likely is caused by a second mole
of bromine beginning to add.

Good results are also obtained for d-limonene in carbon
tetrachloride and 1-,2-octene (mixture of isomers) in carbon
tetrachloride and methanol.   Again the results tend to be
slightly low, but are within experimental error for the size
samples involved.   It is assumed that both double bonds of
d-limonene add bromine independently and no observations were
made to indicate anything to the contrary.

Advantages

The indirect method described above possesses some advan-
tages not present in other indirect methods.   A complete

determination of an unsaturate that readily adds bromine can
be performed in three minutes or less. Also no standard solu-
tions are required. A Beer's law plot relating tribromide ion
concentration to absorbance once prepared is the only standard
needed. It is not necessary to determine the unconsumed
bromine, hence this problem is eliminated.

Very small amounts of unsaturation can be determined by
this technique. Figure 5 shows the absorption spectra of
the tribromide ion in 90% acetic acid-10% water. As can be
observed from this plot, the sensitivity of the determination
can be varied by simply changing the wavelength. It is
possible to determine 0.02 μmoles of cyclohexene in carbon
tetrachloride at a wavelength of 270 mμ. The determination
in this case requires two to three times as long, presumably
because the reactants are so dilute.

A continuous record of the course of the reaction is
obtained when this indirect technique is used. Use of this
record allows observation of completeness of reaction and
makes possible easy extrapolation back to zero time if this
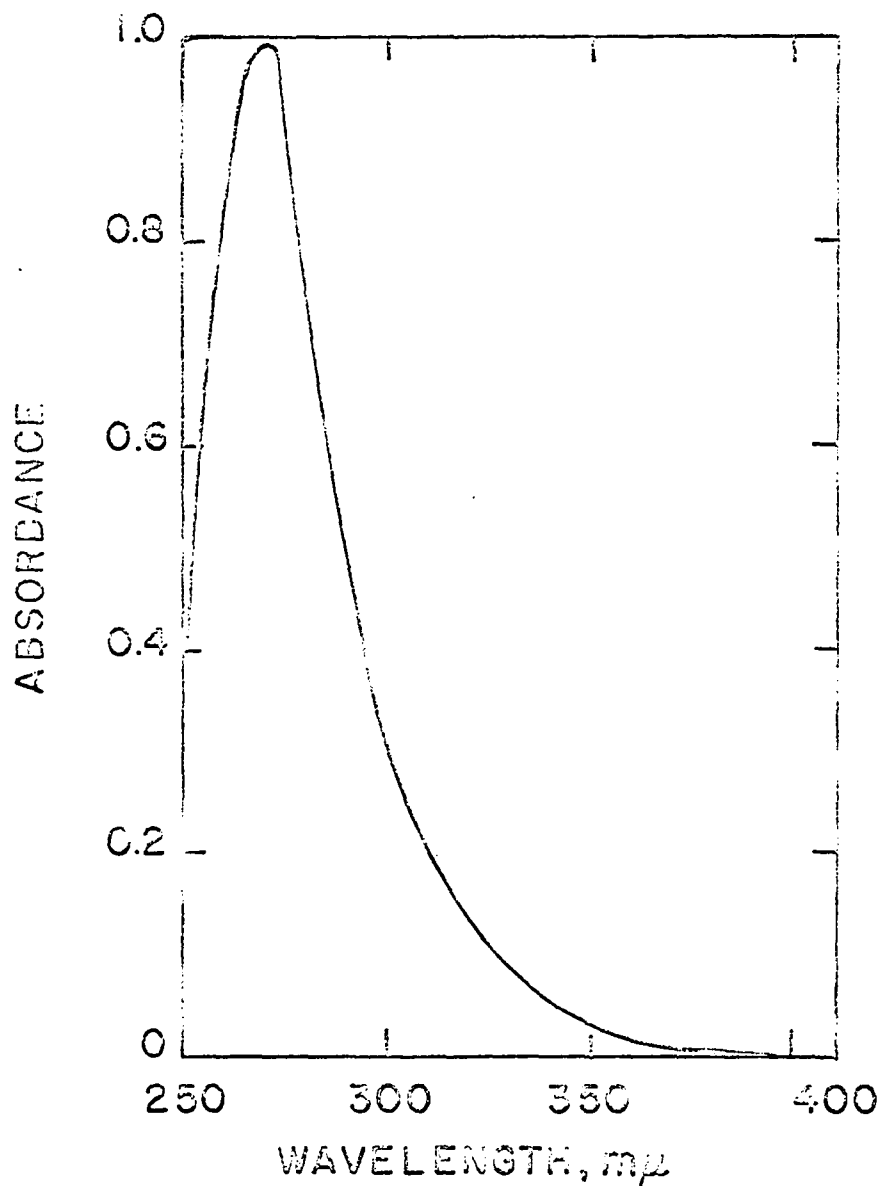becomes necessary.

Fig. 5. Absorption spectra of 3.0×10^{-5} $\underline{M}$ bromine in 90% acetic acid-10% water containing a 6:1 molar ratio of hydrogen bromide to bromine

IDENTIFICATION OF PRODUCTS

Earle and Milner (10), using a methanol solvent, proved
that the reaction solvent participated in the bromine addition
reaction. They isolated some monobromo-monomethoxy compound
in addition to the dibromide and also found that hydrobromic
acid was formed. Bartlett and Tarbell (4) reported this same
reaction earlier.

The formation of hydrobromic acid produced when unsatur-
ates were reacted with bromine in 90% acetic acid-10% water
was discussed above. This hydrobromic acid could be produced
either by the substitution of bromine for hydrogen at a posi-
tion removed from the double bond or by participation of a
solvent anion in the bromine addition reaction.

An attempt was made to determine the products formed when
cyclohexene reacts with bromine in 90% acetic acid-10% water.
This was accomplished according to the following procedure:
An amount of bromine in glacial acetic acid sufficient to just
react with the cyclohexene present was added to the compound
in 90% acetic acid-10% water. The volume of the reaction
solution was then doubled by adding water, and the products
of the addition reaction were extracted into cyclohexane.
After a room temperature evaporation of the cyclohexane, the

reaction products were analyzed qualitatively by mass spec-
trometry.

The results of this analysis showed that only the dibromo
compound and the bromohydrin were present in appreciable
amounts. Bromocyclohexene, which would result from substi-
tution of bromine for hydrogen, and the bromoacetate were not
detected.

FUTURE WORK

With appropriate modifications it should be possible and feasible to adapt or extend either the direct, the indirect, or a combination of the two methods discussed above to automatic or semi-automatic determination of unsaturation. A motor driven buret used in connection with a recording spectrophotometer equipped with a flow through cell might be useful pieces of equipment for this type of analysis. Applications in this area might include such things as the monitoring of production streams where it is desirable to determine certain unsaturates selectively.

An extension of the point-slope technique for spectrophotometric end point location could be useful for routine analysis. The extrapolation of the slope from a single point back to the zero absorbance line might be accomplished electronically.

Improved cell design could result in increased sensitivity and greater convenience for the determination of unsaturation by the indirect method. A cell with a longer path length and a smaller capacity than the one employed will allow smaller samples to be analyzed. This is true because the total amount of tribromide ion present will be reduced, and

a smaller amount of unsaturate will consume a relatively

larger amount of this brominating species thereby causing

a significant absorbance change.

Increased convenience could result from the development

of an internal stirring mechanism for the cells used. Devel-

opment of a new type of cell which would offer easier appli-

cation of an efficient stirring mechanism might be advan-

tageous. A possible approach to the solution of this problem

is the utilization of magnetic stirrers.

SUMMARY

1. The direct titration meth.. is straightforwa.., rapid,
    simple, and accurate for ..e determination o. .lefinic
    unsaturation in most cc.._ounds except those which contain
    strongly electron-withdrawing substituents allylic to the
    double bond or which contain a carbonyl group conjugated
    with the double bond. These latter types of unsaturates
    react very slowly with bromine.

2. If no mercury(II) chloride is employed as catalyst, it is
    possible to titrate compounds which readily add bromine
    in the presence of those compounds which react very slowly
    with bromine. When a mercury(II) chloride catalyst is
    used it is impossible to perform such titrations because
    bromine reacts slowly with the relatively unreactive com-
    pounds during the titration of the fast reacting compounds.

3. The absence of mercury(II) chloride catalyst reduces the
    interference from non-olefinic compounds.

4. For routine analysis of similar samples the end point of
    the direct titration can be determined spectrophoto-
    metrically by recording only one absorbance reading.

5. The indirect spectrophotometric method is rapid, conven-
    ient, and useful for determination of small amounts of

unsaturation.

6. Both methods are adaptable to automated titration procedures.

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