324. *Submicro-methods for the Analysis of Organic Compounds. Part XIX.* Determination of Olefinic Unsaturation*

By R. Belcher and B. Fleet

Olefinic double bonds can be determined on 40—80 μg. of organic material by the addition of a slight excess of standard bromine monochloride, followed by an iodimetric determination of the excess of the reagent. The accuracy of the method varies from ±0·4%, for isolated double bonds and certain less-reactive olefins, to ±3%, for the more-reactive olefins. A modification of the general method is suggested in order to compensate for the interference from substitutive and other side-reactions.

The major problem in the development of a method for the determination of olefinic unsaturation is the wide variation in reactivity of this grouping in different environments. This has resulted in the publication of some 3000 analytical methods to cover the whole range of olefinic compounds. With the exception of certain highly reactive olefins, *e.g.*,

---

* Part XVIII, Belcher, Gawargious, Gouverneur, and Macdonald, *J.*, **1964**, 3560.

the isoprenoids which undergo rearrangement in acid solution, isolated carbon–carbon double bonds can usually be determined satisfactorily by any one of a number of methods; difficulties are only encountered when the double bond is sterically hindered, when it is conjugated to an electron-attracting group, or is part of a conjugated system of double bonds. In the last two examples, the bond-order falls below two.

It was decided to use a halogen-addition method, even though this type of method has certain disadvantages, particularly the lack of specificity; substitution at carbon atoms remote from the double bond occurs to varying degrees, and elimination of hydrogen halide can also occur with certain compounds, particularly highly branched olefins. Interference from enols, aromatic amines, phenols, sulphur compounds, alcohols, etc., is also a complicating factor. A further disadvantage is the failure of all these reagents to react with olefins where the double bond is deactivated, *e.g.*, by conjugation to a strongly electron-attracting group such as CO_2H or CN; hence an entirely different method is required to deal with this class of olefins.

In spite of these disadvantages, halogen addition, from an analytical point of view, is very convenient; hence it is preferred to the more specific hydrogenation and peroxidation reactions, and reliance is placed on a careful control of the reaction conditions in order to keep interferences and side-reactions to a minimum.

Two halogen reagents were examined and compared; first, a solution of bromine and excess of potassium bromide in methanol (tribromide ion Br_3^-),[1] and secondly a solution of bromine monochloride in hydrochloric acid.[2]

Owing to its greater polarity ($\overset{\delta+}{\mathrm{Br}}\text{–}\overset{\delta-}{\mathrm{Cl}}$), bromine monochloride is more reactive towards ethylenic double bonds than is elementary bromine; whereas bromine monochloride adds to the double bond in αβ-unsaturated acids, elementary bromine, under normal analytical conditions, only adds very slowly, so that it is necessary to convert the acid into the carboxylate anion. When elementary bromine is used for the analysis of αβ-unsaturated acids, the final volume of solution becomes so large, owing to the neutralisation, that the reaction time is prolonged. With αβ-unsaturated esters, the problem is even more serious, because of the greater concentration of potassium hydroxide required for hydrolysis. Hence, bromine monochloride is to be preferred. Bromine monochloride is formed according to the equation:

$$\mathrm{BrO_3^- + 2Br^- + 3Cl^- + 6H^+ \longrightarrow 3BrCl + 3H_2O}$$

by acidifying a mixture of bromate and bromide (in a mole ratio of 1 : 2) with hydrochloric acid. In the present study, a standard solution of bromine monochloride was generally used, although a procedure in which a standard bromate–bromide solution was used, to form bromine monochloride *in situ* by acidification with hydrochloric acid, was also tried.

Several factors which influence the addition of bromine monochloride to the olefinic double bond were investigated.

Solvent.—For the majority of the αβ-unsaturated acids analysed, bromine monochloride was added to an aqueous solution, and even though the acid was precipitated, the addition was not affected. However, with some of the higher-molecular-weight acids, there was a tendency for the precipitated acid to creep up the walls of the titration vessel. This resulted in very low results. Hence, it was necessary to find a suitable organic solvent, and methanol was found to be satisfactory; by keeping the reaction temperature in the range 0—3°, oxidation of the solvent was minimised. Ethanol, 2-methoxyethanol, and dioxan were also tried as solvents, but were found to be too rapidly oxidised even at 0°. Acetic acid was unsatisfactory; the iodine–starch end-point was poor, and some side-reactions occurred.

Hydrochloric Acid Concentration.—Variation of the hydrochloric acid concentration of the bromine monochloride reagent was found to affect the reaction in two ways. When

[1] Kaufmann, *Z. Unters. Lebensm.*, 1926, **51**, 3.

[2] Schulek and Burger, *Talanta*, 1960, **7**, 41.

the hydrochloric acid concentration was below 1N, a marked decrease in the stability of the bromine monochloride reagent was observed. To establish if this decrease in stability is accompanied by the homolytic dissociation

$$2\text{BrCl} \rightleftharpoons \text{Br}_2 + \text{Cl}_2$$

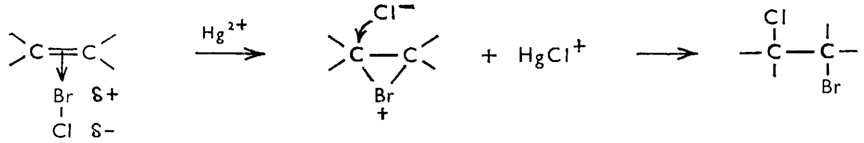
the ultraviolet spectra of solutions containing various concentrations of hydrochloric acid were measured. Elemental bromine gives an absorption maximum at 395 mμ, whereas the characteristic peak for bromine monochloride is found at 340 mμ. No elemental bromine was detected, even with hydrochloric acid concentrations as low as 0·08N.

The increase in the stability of the bromine monochloride solution with increasing hydrochloric acid concentration can be attributed to the formation, in part, of the BrCl_2^- ion.

Catalysis by Mercuric Ions.—The hydrochloric acid concentration of the bromine monochloride reagent also affected the reaction rate with those samples which required the addition of mercuric ion as a " catalyst." It was found necessary to add sufficient mercuric sulphate or perchlorate to convert all the free hydrochloric acid into $[\text{HgCl}_4]^{2-}$ before any catalytic effect could be observed. Thus, with concentrations of hydrochloric acid above 4N, the total ionic concentration after the addition of the mercuric salt was so high that it had a deleterious effect on the starch end-point in the final iodimetric titration of the excess of bromine monochloride. The hydrochloric acid concentration of the standard bromine monochloride solution was, therefore, maintained at 2N. Numerous published methods [3,4] have described the addition of a metal salt to accelerate the addition of halogens, but very few have given any explanation of its mode of action. It has been postulated [5] that the molecule of bromine monochloride undergoes heterolysis:

$$\text{BrCl} + \text{Hg}^{2+} \longrightarrow \text{HgCl}^+ + \text{Br}^+$$

This mechanism appears very unlikely for the following reasons. (i) Attack by Br^+ on a carbon–carbon double bond would be affected only very slightly by the nature of the olefin molecule; hence there would be very little variation in the rate of addition to different compounds. In the present study, quite significant variations in the reaction time were observed, even for two related compounds such as maleic and fumaric acids. (ii) The physical methods used to prove the existence of the simple iodine cation, I^+, have not been successful in demonstrating the existence of Br^+.[6] (iii) The enhanced reactivity of bromine monochloride towards olefinic double bonds cannot be considered as evidence for the existence of the simple Br^+ cation. On the grounds of reactivity alone, it would be very difficult to distinguish between Br^+, H_2OBr^+ (the conjugate acid of hypobromous acid HOBr, where the O–Br bond is covalent), and $\overset{\delta+}{\text{Br}}\text{–}\overset{\delta-}{\text{Cl}}$ where the already considerable polarity is increased by the presence of Hg^{2+} ions. It would therefore appear that the mechanism of addition of bromine monochloride to the olefinic double bond is as follows:



The function of the mercuric ion is to assist in the breaking of the Br–Cl bond. The reaction, $\text{BrCl} + \text{Cl}^- \longrightarrow \text{BrCl}_2^-$, cannot assist in this heterolysis, for there is already a twenty-fold excess of chloride ion in the solution. This mechanism is only valid for the less reactive olefins; several of the more-reactive olefins form stable addition compounds with the mercuric ion, with the result that the addition of bromine monochloride to the

---

[3] Francis, *Ind. Eng. Chem.* (*Analyt.*), 1926, **18**, 821.
[4] Lucas and Pressman, *Analyt. Chem.*, 1938, **10**, 140.
[5] Schulek and Burger, *Talanta*, 1959, **2**, 280.
[6] Arotsky, Mishra, and Symons, *J.*, 1962, 2582.

double bond in these molecules is slowed down by the presence of mercuric ion. This was observed for the addition of bromine monochloride to the double bond in 3,6-methylene-Δ^4-tetrahydrophthalic acid. The catalytic effect of mercuric ion was most marked in the addition to $\alpha\beta$-unsaturated acids, which would suggest that there might be some reduction in the deactivating effect of the carboxyl group, owing to co-ordination with the mercuric ion. The strong acid medium used, however, makes this suggestion open to criticism.

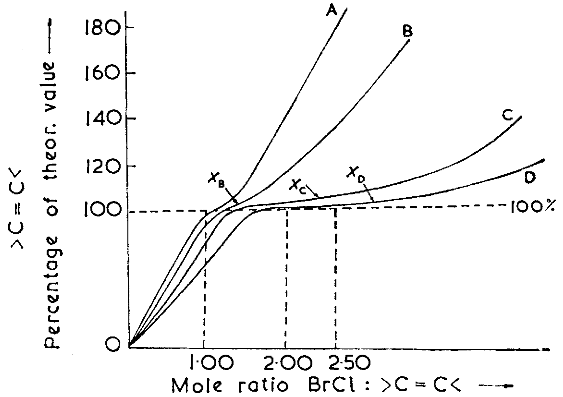


FIGURE 1. Percentage bromination with increasing excess of reagent. A, Cinnamic acid + Hg^{2+}. B, *trans*-Stilbene. C, Cinnamic acid. D, Maleic acid + Hg^{2+}

The presence of mercuric ions, as well as enhancing the rate of addition to double bonds, also increases the rate of substitutive side-reactions; thus, many aromatic-containing olefins give very high results when the addition is carried out in the presence of mercuric ions. Curve A in Figure 1 illustrates this effect for cinnamic acid (curve C shows the course of the addition in the absence of mercuric ion).

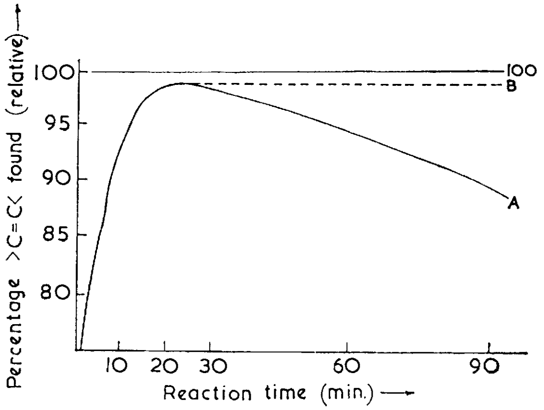


FIGURE 2. Rate curve for the addition of BrCl to cinnamic acid in methanol solution at 0°. A, Blank determinations carried out simultaneously with sample. B, Arbitrary blank value taken when [BrCl] = half of initial concentration

It was found that, with samples which required a fairly long reaction time (*ca.* 1 hr.) in methanolic solution, low results were obtained. These low results were found to be due to the different amounts of bromine monochloride in the sample and " blank " solutions Thus, the amount of oxidation of the solvent by the bromine monochloride was far greater in the " blank " solution than in the sample solution. When an arbitrary blank value was taken, the results obtained were in close agreement with the theoretical values. It should be possible, from a knowledge of the second-order rate equations for the reaction of bromine monochloride with the olefinic compounds, and of bromine monochloride with methanol, to calculate the amount of bromine monochloride that had reacted with the methanol, and so obtain an accurate value for the blank titration. In practice, this is far too complicated, for too many variable factors affect the result, and a separate calculation is required for each different sample weight. Satisfactory results were obtained by titrating the blank solution at a time when one-half of the original bromine monochloride in the sample solution had been consumed. The results of such an experiment are shown in Figure 2.

In Tables 1—4 are summarised the results for the different types of olefinic compound

TABLE 1

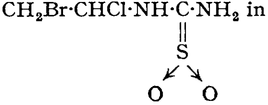
αβ-Unsaturated compounds

Compound	$>C=C<$ (%), found
Maleic acid (theor. $>C=C<$ 20·69%), 1 hr. Hg^{2+} (error 1%)	20·27, 20·67, 19·95, 21·08, 20·37, 20·79, 19·67, 20·71, 20·55, 21·18, 20·48, 21·72
Fumaric acid (theor. 20·69%), $1\frac{1}{4}$—$1\frac{1}{2}$ hr. Hg^{2+} (error ±0·8%)	20·32, 20·01, 20·44, 20·36, 21·50, 20·73
Cinnamic acid (theor. 16·21%), 30 min. MeOH soln. (error ±0·7%)	15·77, 16·19, 15·80, 16·03, 15·93, 15·68, 16·03, 16·06, 16·86
Crotonic acid (theor. 27·90%), $1\frac{1}{2}$ hr. Hg^{2+} (error ±0·8%)	28·15, 28·04, 27·12, 27·98, 27·40, 28·46
Itaconic acid (theor. 18·46%), 1—$1\frac{1}{2}$ hr. Hg^{2+} (error ±0·6%)	18·26, 18·54, 18·76, 18·24, 17·83, 18·85
p-Nitrocinnamic acid (theor. 12·44%), 2—$2\frac{1}{2}$ hr. MeOH soln. (error ±1·4%)	11·08, 13·72, 13·77, 12·68, 11·38, 12·00, 11·31, 11·13
ββ-Dimethylacrylic acid (theor. 25·52%), 2—$2\frac{1}{2}$ hr. MeOH soln. (error ±1·8%)	25·85, 22·74, 27·36, 27·13, 26·03
Cinnamaldehyde (theor. 18·17%), 15—30 min. MeOH soln. −9° (error ±1·3%)	18·47, 18·70, 17·64, 18·33, 19·26, 19·47
Acrolein (theor. 42·84%), 15 min. MeOH soln. −9° (error ±2·8%)	40·06, 41·77, 41·47, 41·98, 41·90, 41·13

The following compounds were attempted, but the results obtained were unsatisfactory. Dimethyl and diethyl fumarate and benzyl cinnamate gave variable recoveries, up to 80% of the theoretical value, under various conditions of hydrolysis. Hydrolysis in a sealed tube would probably improve the recovery. In the case of benzylideneacetophenone, addition at −9°, to inhibit the reaction with the $>C{:}O$ group, was not satisfactory; high and variable results were obtained

TABLE 2

Isolated olefinic linkages

Compound	$>C=C<$ (%), found
3,6-Methylene-Δ^4-tetrahydrophthalic acid (theor. $>C=C<$ 13·18%), 45—60 min.:	
(i) Standard solution; Hg^{2+} retarded addition	13·01, 13·23, 13·13, 13·06, 13·21, 13·27
(ii) Solid samples [Error: (i) ±0·2%; (ii) ±0·4%]	12·92, 12·80, 12·94, 13·35, 13·30, 13·58
cis-Δ^4-Tetrahydrophthalimide (theor. 15·89%), 1—$1\frac{1}{4}$ hr. MeOH soln. (error ±0·6%)	15·94, 15·97, 16·37, 16·46, 15·68, 15·60
Elaidic acid (theor. 8·50%), 15—30 min. MeOH soln. (error ±0·4%) (sample soluble with difficulty)	8·19, 8·41, 8·33, 8·12, 8·51
*Allylthiourea, $CH_2{:}CH{\cdot}NH(C{:}S){\cdot}NH_2$, reacts with **3** mol. BrCl to give  $CH_2Br{\cdot}CHCl{\cdot}NH{\cdot}\underset{\begin{array}{c}\| \\ S \\ \swarrow\ \searrow \\ O\quad O\end{array}}{C}{\cdot}NH_2$ in MeOH soln. (30 min.)	Consumption of BrCl expressed as a percentage of 6·0 equivalents: 100·4, 101·0, 97·9, 98·0, 102·2, 102·4, 108·5, 108·9

* This experiment illustrates that, in certain cases, it is possible to compensate for interfering side-reactions. With Br_2, this reaction is not quantitative, proceeding only to the sulphoxide stage.

studied; sample weights are in the range 40—90 μg. All the results shown were obtained with olefin samples of known composition; hence it was a simple matter to control the BrCl : $>C=C<$ ratio so that the bromine monochloride was not present in large excess. With samples where the degree of unsaturation was unknown, in order to avoid high results owing to a large excess of bromine monochloride being present, it was necessary to carry out a preliminary investigation, using a series of samples containing various mole ratios of BrCl : $>C=C<$. The results of this investigation were plotted graphically, and, from an examination of the curve, it was possible to obtain an approximate value for the degree of unsaturation. Figure 1 shows the results obtained for three olefins, *trans*-stilbene,

TABLE 3

Conjugated dienes

Compound	>C=C< (%), found
trans-Stilbene (theor. >C=C< 13·33%), 15—35 min. MeOH soln. (error ±0·8%)	12·57, 13·77, 13·10, 13·37, 13·05, 13·16, 14·06, 13·45, 13·93
Triphenylethylene (theor. 9·37%), 1 hr. MeOH soln. (error ±0·7%)	9·71, 10·01, 9·48, 9·45
trans-1,4-Diphenylbuta-1,3-diene (theor. 14·28%), 30—45 min. MeOH soln. (error ±1·3%)	12·98, 13·05, 14·62, 14·78, 13·99
trans,trans-Hexa-2,4-dienoic acid (sorbic acid) (theor. 42·84%), 1¼—2 hr. MeOH soln. (error ±3·0%)	42·33, 40·44, 43·05, 45·88
Stilbœstrol dipropionate (theor. 6·31%), ½—1¼ hr. MeOH soln. error *	12·74, 11·50, 12·30, 11·39, 12·15

* Consumption of 2·0 ± 0·17 moles of BrCl per molecule could be accounted for by elimination of a proton from the intermediate bromonium ion to form a new double bond.

TABLE 4

Vinyl compounds

Compound	>C=C< (%), found
Styrene (theor. >C=C< 23·06%), 5 min. MeOH soln. (error ±0·8%)	22·30, 23·15, 22·78, 22·60, 22·92
N-Vinyl-2-pyrrolidone (theor. 21·61%), 15—30 min. MeOH soln. —9° (error ±1·3%)	22·41, 22·02, 22·65, 22·73, 22·63, 22·91
4-Vinylcyclohexene (theor. 44·41%), 15—40 min. MeOH soln. (error ±3·4%)	45·83, 47·07, 46·10, 44·80, 45·52, 47·87

2-Vinyl-1,3-dioxan in MeOH solution at —9° gave results which corresponded to between 110 and 130% of the theoretical value.

cinnamic acid, and maleic acid. The initial steep portion in all three curves shows that all the bromine monochloride was consumed. This is followed by a fairly flat portion, corresponding to complete bromination. The mole ratio BrCl : >C=C< which marks the start of the flat portion depends on the reactivity of the olefin and also on the concentration of the bromine monochloride.

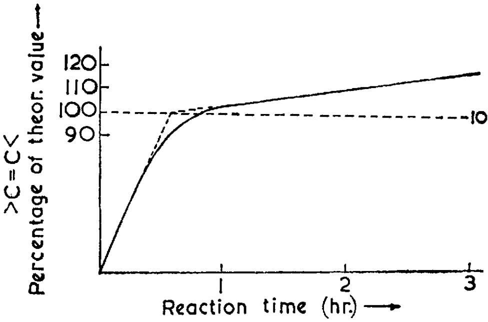


FIGURE 3. Rate curve for the addition of BrCl to maleic acid in aqueous solution

At higher reagent : olefin ratios, the graph begins to ascend. The slope of this final portion depends upon the extent of the side-reactions which, for the purpose of this study, can be referred to as "over-bromination." It can be seen that, with the less reactive olefins, a BrCl : >C=C< ratio of 4 : 1 only gives a relative error of 10%, whereas with the more reactive olefins, an error of 200 or 300% can occur.

From the results of this preliminary investigation, it was possible to plot a rate curve, in order to obtain an accurate value for the degree of unsaturation. Samples with BrCl : >C=C< ratios corresponding to a point (x_B, x_C, x_D) midway along the flat portions of the curves in Figure 1 were allowed to react for various lengths of time. The results for maleic acid are shown in Figure 3; extrapolation of the two straight portions of the curve gave an accurate value for the degree of unsaturation.

To summarise, bromine monochloride is an effective reagent for determining the degree of unsaturation in a wide variety of olefins. The reagent, prepared as described below, changed its titre by only 1% over three months. Two precautions are necessary. First, control of the excess of the reagent to within 20—100%, in order to avoid high results. Secondly, care in the use of a mercuric salt as a catalyst; although advantageous in many cases, it must only be used when it is certain that there are no substitutive or other side-reactions which would also be accelerated.

EXPERIMENTAL

Reagents.—Bromine monochloride (0·1N). 2·7835 g. of AnalaR potassium bromate and 3·9670 g. of AnalaR potassium bromide were dissolved in 250 ml. of water in a 1-l. volumetric flask. The solution is cooled in ice, 200 ml. of concentrated hydrochloric acid (M.A.R. grade) added, and the solution diluted to 1 l.

Sodium thiosulphate 0·01N. 2·4819 g. of M.A.R. $Na_2S_2O_3,5H_2O$ was dissolved in 1 l. of boiled-out distilled water to which a few mg. of sodium carbonate had been added. The solution was standardised against potassium hydrogen di-iodate.

Other reagents. The potassium iodide solution (15%) was prepared every two or three days. The Thyodene indicator was used as the solid reagent. The methanol was an AnalaR reagent.

Apparatus.—The microgram balance (Oertling model QO1) and titration assembly were as previously described.[7] The titration vessel was as previously described.[8]

Procedure.—The weighed sample was transferred from the platinum boat into the titration vessel and dissolved in one or two drops of 1N-sodium hydroxide (for the majority of αβ-unsaturated acids), or in 0·2 ml. of methanol. Before the addition of the bromine monochloride, the sample solution was cooled in ice. A volume of 0·1N-bromine monochloride solution was then added from a micrometer syringe, so that an excess of between 20 and 100% was present (usually between 0·02 and 0·10 ml.). The solution was allowed to stand in a desiccator containing ice until the reaction was complete. In this way, the temperature was maintained at 9—10°. By lowering the titration vessel until it was in contact with the ice, the reaction temperature could be lowered to 0°, and similarly by substituting an ice–salt mixture, the temperature of the reaction could be lowered still further to −9°.

Distilled water (0·5 ml.) was then added to the titration vessel, and the solution cooled in ice again for a further 30 sec. A glass-covered rotor was added and the tip of the micrometer containing the standard 0·01N-thiosulphate was placed in the solution before the final addition of 2 drops of 15% potassium iodide solution was made. In this way the losses due to the volatility of the liberated iodine were minimised. The solution was titrated to a very pale yellow colour, a few mg. of thyodene was added, and the titration was continued until the disappearance of the blue colour.

With the majority of αβ-unsaturated acids, a solution of mercuric sulphate was added. After the addition of the bromine monochloride reagent, a volume of 0·5M-mercuric sulphate solution, equal to one and a half times the volume of the bromine monochloride reagent, was added. This also necessitated the addition of sufficient potassium iodide solution to convert all the free mercuric ion to $[HgI_4]^{2-}$ before the titration of the excess of the bromine monochloride.

We thank the Office of Research and Development, U.S. Department of the Army, which, through its European Research Office, supplied financial support.

CHEMISTRY DEPARTMENT, UNIVERSITY OF BIRMINGHAM,
EDGBASTON, BIRMINGHAM 15.

[*Received, July 7th*, 1964.]

---

[7] Belcher, Gouverneur, and Macdonald, *J.*, 1962, 1938.
[8] Belcher and Fleet, *J.*, 1963, 5720.