DISCUSSION
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Preliminary studies

Halogen cyanides \((XCN)\) are only slightly soluble in water. Their aqueous solutions do not react with iodide, thiosulphate or sulphite even on long standing which is in keeping with the predominantly covalent character of these molecules. In alkaline medium, halogen cyanides get dissolved forming cyanate and halide ions \((1, 122)\):

\[
XCN + 2 OH^- \rightarrow CN^- + X^- + H_2O
\]

However, their behaviour in acidic medium is observed to be different. Williams (2) has mentioned that bromine cyanide dissolves in concentrated mineral acids without undergoing decomposition. Gossin (133) has reported that concentrated sulphuric acid causes liberation of iodine from iodine cyanide.

Concentrated hydrochloric acid has no action in cold while the solution assumes an orange colour on warming due to the formation of iodine(I) chloride which may be obtained in almost quantitative yield upon distillation (134). It is observed during the present studies that the solutions of iodine cyanide and bromine cyanide in dilute mineral acids are colourless indicating thereby that there is no formation of the corresponding iodine or bromine salts.

The liberation of monopositive halogen on dissolution of iodine and bromine cyanides in dilute mineral acids is inferred
In the present studies because iodine and bromine cyanides react with various reducing agents in the presence of dilute hydrochloric, sulphuric, nitric or hydriodic acid,

\[
\text{XCN} + \text{H}^+ \rightleftharpoons \text{HCN} + \text{X}^+
\]

The removal of \( \text{X}^+ \) from the solution by a reductant displaces the equilibrium quantitatively to the right. It may be mentioned that iodine(1) chloride and bromide have already been used as volumetric oxidants in the presence of corresponding acids (125,136); the function of the acid being to liberate \( \text{I}^+ \) from the interhalogen molecule. Acidic iodine cyanide solution is expected to behave similarly (118,127-139) and to be stable as Schulek (122) has reported that even bromine cyanide is stable in weakly acidic solutions.

In the present studies, there is no indication of the formation of \( \text{Cl}^+ \) on dissolving chlorine cyanide in dilute mineral acids as it does not oxidise potassium iodide, sodium sulphite and \( \text{KI}^{\text{II}} \) chloride. On the other hand, it is reported to polymerise in the presence of hydrochloric acid (1,2).

The formation of monopositive halogen from iodine cyanide and bromine cyanide in the presence of glacial acetic acid as well as 1:1 glacial acetic acid - acetic anhydride mixture is also inferred. Iodine cyanide and bromine cyanide dissolve in several nonaqueous donor solvents through the formation of a weak covalent bond between the halogen cation and the donor
atom of the solvent molecule (83). Since iodine is more electro-
positive than bromine, the covalent bond in case of iodine cyanide
and a donor solvent is stronger than that for bromine cyanide.
Thus iodine cyanide acquires a more polar character.

Stability of solutions

The stability of the solutions of iodine cyanide and bromine
cyanide in 0.1M hydrochloric acid, 0.1M sulphuric acid, 0.05M nitric
acid, glacial acetic acid, 1.1 acetic acid – acetic anhydride mixture,
methanol, ethanol, acetone, ethyl acetate and acetonitrile are
studied by measuring the potential of the solution and/or by titrating
with thiosulphate, from time to time. It is observed that the
solutions are stable and do not undergo decomposition or a change
in reactivity with time. The titre does not change by more than
one per cent in any of these media even after two months indicating
their suitability for redox titrimetric determinations. However,
it is recommended that their strengths be checked once a week.

Iodine cyanide solution decomposes on heating and becomes
yellow due to the formation of iodine. It is preferably stored
in dark and in coloured glass bottles as otherwise it acquires a
yellowish tinge after two weeks or so. Iodine cyanide and bromine
cyanide are volatile like the halogens and the other halogenoids,
and escape from the solution at higher temperature.

Redox potential

Unlike iodine cyanide, bromine cyanide is found to act as a
volumetric oxidant in acidic aqueous medium only in the presence
Dependence of redox potential of iodine cyanide on molarity of hydrochloric acid.

Fig. 1 - Dependence of redox potential of iodine cyanide on molarity of hydrochloric acid.
of iodide. The univalent bromine cation oxidises iodide to iodine which in turn reacts with the reductants. The xanthates can, however, be directly titrated electrometrically with bromine cyanide without adding iodide (pp. 42-51), indicating thereby that the bromine cation reacts as such and is reduced to bromide. The titration is reversible and quantitative. Thus iodine cyanide and bromine cyanide are titrated potentiometrically with potassium n-propyl xanthate in aqueous medium at pH 5.0 to 5.4 in order to determine their redox potential. The titration of bromine cyanide with xanthate is of considerable importance because it has rendered possible not only the determination of the redox potential of the system Br⁺/Br⁻ but also its comparison with that of the corresponding I⁺/I⁻ redox system. The values obtained are +0.40V and +0.51V respectively. Thus it is evident that the nitrogen atom is the positive end of the dipole in these molecules with decreasing moment in the order, iodine cyanide > bromine cyanide.

The dependence of redox potential of bromine cyanide on acid molarity could not be studied because the reaction with potassium n-propyl xanthate is not quantitative at pH values other than 5.0 to 5.4, and the xanthate is decomposed by higher acid concentrations. However, it has been possible in case of iodine cyanide by titrating it with tin(II) chloride in hydrochloric acid of different molarity and the results are presented in Fig.1.

There is usually only one abrupt change in potential in the potentiometric titrations of iodine cyanide with various reductants
in aqueous medium and it represents the completion of the reaction. If the solution is fairly concentrated and the acid concentration is also high, only then the two different potential changes corresponding to the successive reduction of iodine cyanide to iodine and iodide, are clearly noted. The same titration of iodine cyanide with tin(ll) chloride in 8M hydrochloric acid is utilized to determine the redox potential for the systems $I^+/I_2$ and $I_2/I^-$ and the value is found to be $+0.56$ and $+0.38\text{V}$ respectively. The determination of redox potential for the systems $Br^+/Br_2$ and $Br_2/Br^-$ could not be possible because there is no intermediate formation of bromine in the reaction of bromine cyanide with potassium $n$-propyl xanthate.

Polarographic behaviour

Iodine cyanide and bromine cyanide depolarise the rotating platinum wire indicator electrode in dilute hydrochloric acid medium giving cathodic waves which are concentration dependent. The dependence of $\log i/(i_d-1)$ on the potential is a straight line and corresponds to reversible and two-electron reduction process in either case. The half-wave potential of iodine cyanide and bromine cyanide in $1\text{M}$ hydrochloric acid is $+0.49$ and $+0.37\text{V}$ respectively. The values are too positive to use a dropping mercury electrode. The half-wave potential is independent of the strength of supporting electrolyte indicating the absence of formation of complexes of the type $ICl_2^-$. It may be mentioned that Popov and Jacke (140) have obtained three waves during voltammetric studies of iodine(I) chloride and bromide in acetonitrile for the overall reduction of
these intermediates to iodide. However, specific electrode reactions could not be assigned to the individual waves. The limiting current plateau potential in the polarograms produced due to the cathodic reduction of the halogen cation in the present studies is +0.3 to +0.1V. This potential range and the proportionality of the diffusion current with concentration of halogen cyanides, provide favourable conditions for performing the amperometric titrations using a rotating platinum wire indicator electrode.

It is evident, therefore, that the behaviour of halogen cyanides as cyanides or as halides may not be due to the difference in type of bonding but to the difference in solvent-solute interactions and to the energy relationship involved in ionisation and in the particular reaction. The univalent halogen cation is thus formed during certain reactions though it may not pre-exist in free halogen cyanide molecules. These preliminary studies also help in understanding the mode of reduction of iodine cyanide and bromine cyanide in the absence or presence of a reducing agent and to assess their potentialities as volumetric oxidants. Iodine cyanide and bromine cyanide are thus moderate oxidising agents and their oxidising behaviour can be studied only in acidic aqueous medium or nonaqueous donor solvents. The titration may be followed visually as well as electrometrically. However, chlorine cyanide is found to be iodometrically inactive even in acidic aqueous medium.
Determination of Iodide Cyanide Compounds

Inorganic ions have been determined in aqueous medium with practically all the known oxidants (127-129, 141). However, relatively little work has been carried out on their determination in nonaqueous solvents (142, 143). In the present studies, a few inorganic ions are titrated with iodine cyanide and bromine cyanide with a view to understanding the mode of reduction of halogen cyanides in different media, to assess their potentialities as volumetric oxidants and to establish the conditions for the quantitative reaction of these ions with halogen cyanides in aqueous and nonaqueous media.

Determination of Iodide

Iodine cyanide and bromine cyanide oxidise potassium iodide to iodine in 0.1M hydrochloric acid, 0.05M sulphuric acid or 0.05M nitric acid and the resulting solutions give blue colour with starch. Iodide reacts in aqueous medium with iodine cyanide and bromine cyanide in the molar ratio 1:1 and 2:1 respectively (Tables II and III).

\[ \text{I}^- + \text{I}^+ \rightarrow \text{I}_2 \]
\[ 2 \text{I}^- + \text{Br}^+ \rightarrow \text{I}_2 + \text{Br}^- \]

The reaction is quantitative. The titration is reversible and can be followed either amperometrically or potentiometrically.

In the direct amperometric titration of iodide with iodine cyanide and bromine cyanide at +0.15V (vs SCE), the current is
Fig. 3 - Reverse amperometric titrations of vanadium (II) sulphate (i, ii), tin(II) chloride (iii, iv) and potassium iodide (v, vi) with iodine cyanide (i, iii, v) and bromine cyanide (ii, iv, vi) in aqueous medium.
Fig. 4 – Potentiometric titrations of iodine cyanide (i–iv) and bromine cyanide (x, xii) with tin (II) chloride (i), sodium thiosulphate (ii), arsenic (III) oxide (iii), sodium sulphite (iv, x), mercury (II) perchlorate (v), potassium antimonyl tartrate (vi) and sodium sulphide (xii); of potassium iodide (vii, viii), sodium thiosulphate (ix) and tin (II) chloride (xi) with iodine cyanide (vii) and bromine cyanide (viii, ix, xi) in aqueous medium.
zero to start with, and increases on gradual addition of the oxidant due to the cathodic reduction of the iodine formed. After the equivalence point is reached, the increase in current is relatively less and is due to the cathodic reduction of halogen cation (Fig. 3). In the reverse amperometric titrations, the current starts increasing indicating that the formation of iodine more than compensates the decrease in current due to the corresponding consumption of the halogen cyanide. The current remains constant after the equivalence point (Fig. 3).

The potentiometric titration of iodide with iodine cyanide and bromine cyanide is still more interesting as there is no sudden increase in potential at the equivalence point. Rather it starts increasing from the very beginning and remains constant after the equivalence point (Fig. 4).

Iodine cyanide and bromine cyanide do not react with bromide and thus no electrometric titration could be performed. The reaction is selective for iodide and as little as 2 μg can be determined in 100 times excess of chloride and bromide. Acetate, bicarbonate, sulphate, nitrate, cyanide and iron(II) also do not interfere but the oxalate does. In this respect, the titration of iodide with halogen cyanides exceeds the argentometric determination in its sensitivity and selectivity. The method can also be utilised for the determination of iodide in a mixture with iodine.

Potassium iodide is successfully titrated with these oxidants in glacial acetic acid and 1:1 acetic acid - acetic anhydride.
Fig. 6 – Potentiometric titrations of (i) potassium iodide, (ii) sodium thiosulphate, (iii) sodium sulphite, (iv) arsenic (III) chloride, (v) iron (II) perchlorate, (vi) ammonium thiocyanate, (vii) tin (II) chloride & (viii) antimony (III) chloride with iodine cyanide in 1:1 acetic acid—acetic anhydride mixture.
Fig. 7 - Potentiometric titrations of potassium iodide (I), sodium sulphide (II), sodium sulphite (III), tin (II), chloride (IV), ammonium thiocyanate (V), arsenic (III) chloride (VI), & antimony (III) chloride (VII) with bromine cyanide in glacial acetic acid.
mixture potentiometrically (Figs 5-7). On adding iodine cyanide or bromine cyanide solution to that of potassium iodide, the colour changes through yellow to orange indicating that the iodide is first oxidised to iodine and then to complex tri-iodide ion \( (I_3^-) \). However, there is no abrupt potential change corresponding to the formation of iodine unlike that in aqueous medium. When iodide is completely oxidised to complex tri-iodide ion, there is an abrupt rise in potential at ICN/KI or BrCN/KI molar ratio of 1:2 and 1:3 respectively and the solution acquires a yellowish brown colour which is characteristic of tri-iodide ion in these media (144):

\[
I^+ + 2 I^- \rightarrow I_3^-
\]

\[
Br^+ + 3 I^- \rightarrow I_3^- + Br^-\]

In nonaqueous solvents, the formation of complex tri-iodide ion is possible because of its greater stability in organic solvents than in water (141). Thus in the above titration of iodide with iodine cyanide and bromine cyanide, the change in potential at the molar ratio 2:1 and 3:1 respectively, gradually becomes smaller when acetic acid containing increasing amounts of water is used as a solvent owing to the decreasing stability of tri-iodide ion in the presence of water.

**Potentiation of sulphide, sulphite and thiosulphate**

Sulphide, sulphite and thiosulphate are oxidised quantitatively by halogen cyanides in acidic aqueous medium to sulphur, sulphate and tetrathionate respectively (Tables I-III). A suspension of colloidal sulphur is observed in the titration of sulphide with these
oxidants. A blue colour appears on adding even a drop of reductant solution to that of halogen cyanide containing starch indicator and the colour disappears abruptly at the end point indicating the reduction of the oxidant to halide ion. However, the titrations with bromine cyanide are possible only in the presence of iodide.

The titration of thiosulphate is reversible. But accurate results are not obtained when sulphide and sulphite are taken in the flask and titrated with halogen cyanides, probably due to the aerial oxidation of the reductants and action of acid, if present alone. These reductants are, therefore, titrated in the reverse manner. Since sulphide, sulphite and thiosulphate react with dilute acids, higher concentrations of the acids in the case of these reductants are not advisable. The titrations are possible even in the presence of nitric acid but its total concentration should not exceed 0.05M.

In nonaqueous solvents, sodium sulphite solution becomes yellowish on addition of iodine cyanide and the first potential change occurs at I$_2$/SO$_3^-$ molar ratio of 1:1. On further addition of the oxidant, the iodide produced is oxidised to tri-iodide ion, as is evident from the yellowish brown colour which develops during this part of the titration, and a second change in potential occurs at a molar ratio of 3:2 for I$_2$/SO$_3^-$ . The tri-iodide ion is then converted into iodine, yielding a bright red solution. The change in potential is slow during this part of the titration and there is no sudden change in e.m.f. corresponding to an oxidant/reductant molar ratio of 2:1. However, when this ratio
is exceeded, the curve becomes flat indicating the presence of excess of iodine cyanide (Figs. 5 and 6).

The oxidation of sodium sulphite with iodine cyanide in these solvents is quantitative even in the absence of sodium acetate whereas iodine(I) chloride has been reported to oxidise sodium sulphite quantitatively only in the presence of excess of sodium acetate (145). Thus, iodine cyanide appears to be a better oxidant than iodine(I) chloride though the oxidising behaviour of both the compounds is similar.

Similarly iodine cyanide reacts with thiosulphate in these media in 1:2 molar ratio forming iodide and tetrathionate (Figs. 5 and 6). The solution becomes yellow which gradually changes to orange and then to red.

The behaviour of bromine cyanide in glacial acetic acid and 1:1 acetic acid - acetic anhydride mixture is somewhat different from that of iodine cyanide because there is neither any colour change nor formation of complex ion of the type \( \text{Br}_3^- \) during these titrations. It reacts with sulphite and sulphide in the molar ratio 1:1 forming sulphate and sulphur respectively and itself is directly reduced to bromide (Table IV; Fig. 7). The oxidation of thiosulphate to tetrathionate is its characteristic reaction only with iodine and is thus not possible with bromine cyanide in these media.

determination of sulphide, sulphite and thiosulphate in a mixture

The total concentration of sulphide, sulphite and thiosulphate in a mixture is obtained on titrating with iodine cyanide or bromine
cyanide in aqueous medium (Table VI). Sulphide is separated as zinc sulphide by adding freshly prepared zinc carbonate suspension to the mixture solution and is determined directly from the precipitate whereas the amount of sulphite and thiosulphate in the mixture is obtained on titrating the filtrate. The interference of sulphite is removed by treating the mixture solution with excess of formaldehyde when an inert formaldehyde-bisulphite adduct is formed. It may be mentioned that formaldehyde is not oxidised by halogen cyanides.

determination of thiocyanate

Ammonium thiocyanate reacts with iodine cyanide and bromine cyanide in these nonaqueous solvents in the molar ratio 1:1 and 2:1 respectively (Figs. 5-7) forming thiocyanogen. The reactions may be expressed as below:

\[
\begin{align*}
2 \text{CNS}^- + 2 \text{I}^+ & \rightarrow (\text{CNS})_2 + \text{I}_3 \\
2 \text{CNS}^- + \text{Br}^+ & \rightarrow (\text{CNS})_2 + \text{Br}^-
\end{align*}
\]

The solution becomes yellow due to the evolution of iodine in the titration with iodine cyanide whereas it remains colourless in the other titration. Both the titrations are reversible. However, the titration is not possible in aqueous medium.

determination of iron(II)

Halogen cyanides do not oxidise iron(II) in aqueous medium and the titration could not be carried out even in the presence of EDTA. However, iodine cyanide reacts with iron(II) perborate in 1:1 molar ratio in glacial acetic acid and 1:1 acetic acid - acetic
anhydride media in the presence of anhydrous sodium acetate forming iron(III) (Figs. 5 and 6). The reaction is exothermic and iron(II) solution becomes yellow and then brown on further addition of iodine cyanide because of the formation of iron(III) acetate.

**Determination of tin(II)**

Tin(II) is oxidised with iodine cyanide and bromine cyanide to tin(IV) in aqueous medium and the reaction can be followed visually as well as electrometrically (Figs. 2-4):

\[ \text{Sn}^{2+} + X^+ \rightarrow \text{Sn}^{4+} + X^- \]

There is an abrupt appearance of iodine colour at the end point even in the absence of starch indicator. It is better to carry out the titration of tin(II) in an atmosphere of carbon dioxide or nitrogen to avoid its oxidation with air. The use of boiled water is also recommended. The titration is reversible and is possible over a wide range of acid concentration.

Iodine cyanide oxidises tin(II) to tin(IV) in glacial acetic acid and 1:1 acetic acid - acetic anhydride media in the presence of molar concentration of anhydrous sodium acetate (Table II; Figs. 5 and 6). The colour becomes yellow on the first addition of iodine cyanide and then turns brown. The titration with bromine cyanide is possible even in absence of sodium acetate (Table IV; Fig. 7).

**Determination of vanadium(II)**

Vanadium(II) reacts with iodine cyanide or bromine cyanide in the molar ratio 2:1 in aqueous medium in an inert atmosphere of
Carbon dioxide or nitrogen is oxidised to vanadium(III). The titration is possible over a wide range of acid concentration and is carried out visually as well as electrometrically. It may be mentioned that the electrometric titrations of vanadium(II) cover the wider range of its concentration whereas it can be determined visually with halogen cyanide using starch indicator only in very dilute solutions (Table I). In concentrated solutions, the end point cannot be accurately noted due to the violet colour of vanadium(II) itself. In such cases, it is possible to add a known excess of the oxidant to vanadium(II) and back titrate the excess with \text{tim(II)} when the end point is marked by the disappearance of the violet blue colour. During the electrometric titration, the violet colour of vanadium(II) starts fading and becomes yellowish through blue at the equivalence point. The colour becomes reddish yellow when excess of iodine cyanide is added. Iron(II) does not affect the accuracy and the course of the reaction, and as little as 0.1 mg of vanadium(II) can be electrometrically determined with halogen cyanides in 40 times excess of iron(II).

Amperometric titrations of vanadium(II) and \text{tim(II)}

In the direct amperometric titrations of vanadium(II) and \text{tim(II)} with iodine cyanide and bromine cyanide in aqueous medium at +0.16V (vs SCE), the current is practically zero in the beginning and remains constant until the end point is reached when it starts increasing gradually due to the cathodic reduction of the unconsumed iodine cation and the evolved iodine respectively, resulting in a straight line plot (Fig. 2).
Fig. 8 - Biamperometric titrations: iodine cyanide with tin (II) chloride (i), tin (II) chloride with iodine cyanide (ii); Bipotentiometric titrations: tin (II) chloride with iodine cyanide (iii), iodine cyanide with tin (II) chloride (iv) and potassium n-propyl xanthate (v), potassium n-propyl xanthate with iodine cyanide (vi) & bromine cyanide (viii), bromine cyanide with potassium n-propyl xanthate (vii)

Reductant/oxidant (i,iv,v,vi); Oxidant/reductant (ii,iii,vi,viii), molar ratio
In the reverse amperometric titrations of these metal ions with bromine cyanide, the current due to the cathodic reduction of the evolved iodine, decreases linearly on adding the reductant solution till the equivalence point is reached after which it remains constant indicating the completion of the reaction (Fig. 3).

The shape of the reverse amperometric titration curves of these ions with iodine cyanide is, however, neither the one commonly obtained (146,147) nor similar to that in the corresponding titrations of bromine cyanide. The initial current due to the reduction of iodine cation, starts increasing instead of decreasing as the titration proceeds until half of the theoretically required amount of the reductant has been added. During these titrations, the xanthates reduce iodine cyanide to iodide which in turn reacts with the un consumed oxidant forming iodine and thereby imparting yellow colour to the solution. The increase in current is attributed to the formation of iodine which more than compensates the decrease in current intensity due to corresponding consumption of iodine cyanide. With concentrated solutions, the plot is not a straight line and the half equivalence point is located by extrapolation. When iodine cyanide has been completely converted into iodine, the current starts decreasing gradually and linearly and assumes zero value at the equivalence point. On further additions of the reductant, the current remains constant (Fig. 3).

The above explanation of the increase in current in the reverse titrations with iodine cyanide, is in keeping with the trend of the titration curve of iodine cyanide with iodide in dilute
Hydrochloric acid medium (Figs. 2 and 3) where they react in 1:1 molar ratio forming iodine. However, bromine cyanide could neither be titrated with bromide under similar conditions electrometrically nor there is any colour of bromine in the solution indicating that they do not react in the way iodine cyanide and iodide do. It justifies the different shape of the reverse electrometric titration curves with bromine cyanide.

Biampereometric and bipotentiometric titrations

The curves of direct and reverse biampereometric and bipotentiometric titrations of tin(II) chloride with these oxidants (Fig. 8) are, however, the expected ones for the titrations of an irreversible redox system with the reversible one and vice versa. The titrations are fast, quantitative and simple (Table VIII).

Determination of arsenic(III) and antimony(III)

Arsenic(III) oxide and potassium antimonyl tartrate quantitatively react with halogen cyanides in aqueous medium in 1:2 molar ratio and are titrated in the presence of sodium bicarbonate which destroys hydriodic acid formed during the course of the titrations (Tables I and III). The optimum pH for the complete oxidation with bromine cyanide is found to be 5.8 to 6.4 whereas the pH range 4 to 9 is recommended by Vogel (148) for the corresponding titrations with iodine. The pH need not be so rigidly controlled in the titrations with iodine cyanide. Both the titrations are irreversible.

Iodine cyanide and bromine cyanide do not react with arsenic(III) and antimony(III) chlorides quantitatively in glacial acetic acid and 1:1 acetic acid - acetic anhydride mixture as is evident from
The fact that there is neither a measurable heat of reaction nor a change in colour on mixing the reactants. However, the oxidation is complete in solutions which are molar or of higher concentration with respect to sodium acetate. Sodium acetate which is a strong base in these media, reduces the high potentials of the arsenic and antimony couples and, thereby, renders the titrations possible. The reactions of iodine cyanide with these reductants proceed with the evolution of a considerable amount of heat. Arsenic(III) and antimony(III) reduce iodine cyanide to elementary iodine as indicated by the red colour of the solution and change in potential at oxidant/reductant molar ratio of 2:1 (Figs. 5 and 6). Bromine cyanide is, however, reduced to bromide and there is an abrupt change in potential at SbCl$_3$/BrCN and AsCl$_3$/BrCN molar ratio of 1:1 (Fig. 7). There is another potential change in the titration of iodine cyanide with arsenic(III) chloride at I$_2$/As(III) molar ratio of 3:2 and may be attributed to the formation of tri-iodide ion:

$$2 \text{As}^{2+} + 3 \text{I}^- \rightarrow 2 \text{As}^{5+} + \text{I}_3^-$$

There is no such change in potential in the titration with antimony(III) probably due to relatively high redox potential of Sb(III)/Sb(V) system. The titrations in nonaqueous media are reversible.

**Determination of mercury(II)**

Mercury(I) perchlorate reduces iodine cyanide to iodide and itself is oxidised to mercury(II) in aqueous as well as nonaqueous media (Tables I and II). In aqueous medium, the solution should
To almost free from mineral acids otherwise a white precipitate appears on addition of a drop of iodine cyanide solution. The titration is, therefore, carried out in the presence of sodium bicarbonate. Potassium iodide is added to iodine cyanide to make the end point sharp otherwise a bright yellow colour appears which changes to yellowish green and renders the detection of end point somewhat difficult. Mercury(I) cannot be titrated directly with bromine cyanide in aqueous medium because bromine cyanide acts as an oxidising agent only in presence of iodide which, in the present case, precipitates out mercury(I) as mercury(I) iodide.

determination of silver, mercury(I), mercury(II) and lead(II)

Silver nitrate, mercury(I) perchlorate, mercury(II) acetate and lead(II) nitrate react with excess of iodide forming insoluble iodides and their amount is indirectly determined by titrating the unconsumed iodide with iodine cyanide or bromine cyanide (Table V). Similar method may be adopted for any metal ion which forms insoluble iodide. Furthermore, it has led to a novel and easy method of estimating a mixture of mercury(I) and mercury(II). The total amount of these ions is obtained by this method and the amount of mercury(I) in the mixture is determined by titrating with iodine cyanide (Table VII).

In case of lead(II) nitrate, the precipitate of lead iodide dissolves in sodium hydroxide forming sodium plumbite and iodides:

\[
Pb(NO_3)_2 + 2 KI \rightarrow PbI_2 + 2 KNO_3
\]

\[
PbI_2 + 4 NaOH \rightarrow Na_2PbO_2 + 2 NaI + 2 H_2O
\]
The solution is acidified with dilute nitric acid and then potentiometrically titrated with the halogen cyanide solution in glacial acetic acid or 0.05M nitric acid.

\[ \text{NaI} + I^+ + \text{CN}^- \rightarrow \text{NaCN} + I_2 \]
\[ 2 \text{NaI} + \text{Br}^+ + \text{CN}^- \rightarrow \text{NaBr} + \text{NaCN} + I_2 \]

However, nitric acid concentration in the resulting solution should not exceed 0.05M.

**Determination of manganese dioxide**

Manganese dioxide oxidises ascorbic acid at room temperature quantitatively to dehydroascorbic acid. The unconsumed ascorbic acid is titrated against halogen cyanide (Table V). Lead dioxide does not react with ascorbic acid solution and hence could not be determined by this method.

**Determination of titanium(III) chloride**

Titanium(III) chloride reacts slowly with these oxidants in 2:1 molar ratio in 0.1M hydrochloric acid solution in an atmosphere of nitrogen or carbon dioxide (Tables I and III):

\[ 2 \text{Ti}^{3+} + X^+ \rightarrow 2 \text{Ti}^{4+} + X^- \]

Chalík (140) has reported that titanium(III) can be titrated with iodine(I) chloride over a wide range of acid concentrations. However, the reaction of titanium(III) with halogen cyanides is dependent upon acid concentration and is not quantitative if the solution is molar with respect to acid. Even in 0.1M hydrochloric acid, the reaction is too slow to be followed by a direct titration. The presence of EDTA shifts the equilibrium in the forward direction.
by forming a stable insoluble complex with titanium(IV) (150).

Role of cyanide ion

Iodine cyanide and bromine cyanide dissolve in dilute mineral acids yielding the well-known complexing cyanide ions. An attempt is, therefore, made to exploit the complexing nature of cyanide ions in shifting the equilibrium in the forward direction in titrations of metal ions such as iron(II), copper(I), titanium(III), etc., which do not otherwise proceed to completion. However, even the addition of excess cyanide ions does not serve the purpose and thus EDTA has to be added in titrations of titanium(III) with these oxidants. The titration of iron(II) is not possible even in presence of EDTA. In case of the titration of copper(I), on the other hand, the presence of cyanide has a reverse effect as it reduces copper(II) back to copper(I) and then forms stable cuprocyanide complexes (151).

Indicators

Starch works successfully as an indicator in the visual titrations. Since bromine cyanide acts as an oxidant in aqueous medium in the presence of iodide only and there is no intermediate formation of bromine even if excess of bromide is added, the indicators such as methyl orange, indigo carmine, crystal violet and malachite green which mark the end point due to their destruction by the bromine formed by one drop in excess of the titrant, could not be used.

Carbon tetrachloride, chloroform, carbon disulphide and benzene are also used as extraction indicators in place of starch.
in the titrations of halogen cyanides with sulphide, sulphite, thiocyanate and tin(II). The end point is marked by the appearance or disappearance of the iodine colour in the organic solvent layer, as the case may be. Some suitable indicator for visual titrations in acetic acid could not be found.

Interferences

The presence of ions such as sodium, potassium, calcium, strontium, barium, magnesium, zinc, lanthanum(III), iron(II), chloride, bromide, sulphate, nitrate, acetate and oxalate does not interfere in these titrations. However, the titrations could not be carried out in the presence of copper(II) and lead(II) since copper(II) liberates iodine from iodide and lead(II) forms yellow precipitate of lead(II) iodide. The presence of silver(I), mercury(I), mercury(II) and other metal ions which form insoluble iodides, render the detection of end point difficult particularly in the titrations with bromine cyanide in aqueous medium. The precipitate formed is filtered off before titration in such cases. Carbonate interferes due to its reaction with iodine.

Conclusion

It is evident from these studies that redox reactions of iodine cyanide and bromine cyanide are the reactions of non-positive halogen. Thus the so-called cyanogen halides have halogen atom as the positive end of the dipole of the molecule in the acidic medium and the manner in which iodine cyanide or bromine cyanide ionises, is not a function of the structure alone but also of the
environments. The use of the nonaqueous solvents suggests that the formation of iodine(I) chloride is not a pre-requisite for iodine cyanide to function as an oxidant. The role played by the acid is only in liberating the halogen cation and glacial acetic acid or any of the mineral acids may be employed for this purpose. However, the concentration of nitric acid should not be more than 0.05M. In aqueous medium, the acid concentration should be more than 0.04M otherwise the colour change is not sharp, and iodine cyanide and bromine cyanide are not completely ionised. On the other hand, starch becomes ineffective at acid concentrations higher than 4M.

In the redox reactions of iodine cyanide with various inorganic ions, the monopositive iodine is reduced to iodine by a reductant of fairly high redox potential and to iodide by one of low redox potential, followed by oxidation of iodide to iodine by more iodine cyanide. The final product of reduction of iodine cyanide is, therefore, dependent upon the entire system involved. However, bromine cyanide acts as an oxidising agent in aqueous medium only in the presence of iodide and is directly reduced to bromide. There is no intermediate formation of bromine. Only those reactions which entail the reduction to iodide, can be followed by direct visual titrations in aqueous medium.
Determination of Xanthates

The chemistry of organic sulphur compounds seems to have started from the date Neise (152) reported the formation of xanthic acid and its salts. Reid (153) as well as Whitemore and Lieber (154) have surveyed the earlier literature on the determination of xanthates. The oxidation of xanthate with copper(II) ions, one of the first reactions to be studied, is used as the basis for the determination of xanthates both volumetrically (155,156) and gravimetrically (157). Maurice (158) has determined ethyl xanthate with copper(II) acetate potentiometrically. But Linch (159) considers the titrations with copper and other heavy metals, to be un Dependable owing to the formation of basic salts and co-precipitation. Ammonium persulphate, chloramine T, hypochlorous acid and a number of other oxidants have also been used (155). These methods require more technique and time than is ordinarily desirable.

Delachanal and Hermet (160) were the first to propose the direct titration of xanthate with iodine which is easier and quicker than the methods mentioned above. The operations such as precipitation, allowing the reactants to stand for several hours to ensure complete precipitation, filtering and washing required in earlier methods, are completely eliminated. Hatuszak (161), and Susuf and Khundkar (162) have critically reviewed the different procedures developed by various workers. Hatuszak (161) has suggested the use of iodate in the presence of excess iodide in place of iodine. Susuf and Khundkar (162) have titrated xanthates with iodine using sodium acetate buffer to control the hydrogen
Fig. 9 - Potentiometric titrations of (i) methyl xanthate, (ii) ethyl xanthate, (iii) n-propyl xanthate, (iv) iso-propyl xanthate, (v) allyl xanthate, (vi) n-butyl xanthate, (vii) t-butyl xanthate, (viii) iso-amyl xanthate & (ix) benzyl xanthate with iodine cyanide in aqueous medium.
ion concentration. It may be mentioned that most of the methods have been developed for the determination of carbon disulphide after being converted to xanthate. Little work has, however, been reported on the determination of xanthates using other halogen compounds as oxidants, especially in nonaqueous media (130, 153).

In the present studies, methyl, ethyl, n-propyl, isopropyl, n-butyl, t-butyl, allyl, isomyl, cyclohexyl and benzyl xanthates of potassium (KOC₅S₂K) are titrated visually and electrometrically with iodine cyanide and bromine cyanide. They react with these oxidants in the molar ratio 2:1 in aqueous medium at pH 5.0 to 5.4 (Table IX). Thus the xanthates of isomeric alcohols react with these oxidants in the same molar ratio. Starch works quite satisfactorily as a visual indicator. The first drop of the oxidant in excess gives a violet to blue colour at the end point. It is evident from these facts that the halogen cation undergoes two electron change and is reduced to the corresponding halide ion. The reactions may be represented by the following general equations:

\[
\begin{align*}
2 \text{R-O-C-S-K} + \text{I}^+ + \text{H}^+ & \rightarrow (\text{R-O-C-S})_2 + 2 \text{K}^+ + \text{I}^- + \text{HCN} \\
\text{BrCN} + 2 \text{H}^+ + 2 \text{I}^- & \rightarrow \text{I}_2 + 2 \text{H}^+ + \text{CN}^- + \text{Br}^- \\
2(\text{R-O-C-S-K}) + \text{I}_2 & \rightarrow (\text{R-O-C-S})_2 + 2 \text{K}^+ + 3 \text{I}^-
\end{align*}
\]

The oxidation product, dixanthogen (153), is insoluble in water and appears as a white suspension or emulsion depending upon the concentration of the reactants. It has been separated in some cases and its composition ascertained by elemental analysis.
Potentiometric titrations of (i) methyl xanthate, (ii) ethyl xanthate, (iii) n-propyl xanthate, (iv) iso-propyl xanthate, (v) allyl xanthate, (vi) n-butyl xanthate, (vii) t-butyl xanthate, (viii) iso-amyl xanthate, (ix) cyclohexanol xanthate, and (x) benzyl xanthate with bromine cyanide in aqueous medium.
It neither reacts with these oxidants nor hinders the detection of end point when starch is used as indicator. Potassium cyclohexyl xanthate is titrated visually with normal ease but unlike the other xanthates, cannot be titrated potentiometrically in aqueous medium.

In all titrimetric determinations using bromine cyanide in aqueous medium, the addition of potassium iodide is found to be essential. However, the electrometric titrations of xanthates with bromine cyanide are successfully carried out in the absence of iodide (Figs. 10 and 11). The reactions are quick as well as quantitative and the changes in potential at the equivalence point are fairly large. In visual titrations, the addition of potassium iodide is essential for detecting the end point because of the nonavailability of a suitable specific indicator. Crystal violet, methyl orange, indigo carmine and malachite green which mark the end point due to their destruction by the free bromine formed by the first drop in excess of the titrant, could not be used as indicators in these titrations even in the presence of excess bromide. Unlike $I^+$ and $I^-$, $Br^+$ and $Br^-$ do not react to form free bromine under these experimental conditions. It is evident, therefore, that the reaction does not essentially proceed through iodine formation but bromine cation reacts as such with the xanthates without affecting the reaction stoichiometry.

The qualitative oxidation of the xanthates with bromine cyanide in the absence of mineral acids, has been studied by Cambron and Whitby (163) who believed bromine cyanide to be a bromide of cyanogen and thus could not explain the mode of
oxidation. They, however, only referred to the suggestion of ref (164) that it may act as an oxidant due to the probable formation of hypobromous acid on its hydrolysis. In the present studies, the titrations are carried out not only in the presence of mineral acids (Table IX) but also in nonaqueous media (Tables X and XI) where hydrolysis of bromine cyanide does not occur. It is evident, therefore, that the reaction is only due to the existence of bromine cation.

The acid concentration is kept low by diluting the solution with water, and the pH of the solution is not allowed to fall below 5.0 at the equivalence point to avoid acid decomposition of the xanthates which is reported to decrease with increasing molecular weight of the xanthate and decreasing acid concentration (165,166). The stability of aqueous solutions of xanthates is, therefore, a function of pH and the molecular weight of the species under investigation. The use of sodium bicarbonate for neutralising the excess acid in these titrations is not recommended because high results are obtained, probably due to the suppressed ionisation of iodine and bromine cyanides. The visual titrations are successfully carried out using acetate buffer of pH 5.0 to 5.4 but the colour change at the equivalence point is not sharp. Thus the dilution of the solutions with water is considered to be the best to achieve the optimum hydrogen ion concentration. Though the potentiometric determination of xanthates in aqueous medium gives somewhat lower results even up to 1 per cent (Table IX), yet the change in potential at the equivalence point is fairly large (Figs. 9 and 10). The low results are probably due to the presence
of hydrogen ions for longer period which facilitates the formation of less stable xanthic acid.

These titrations are carried out at room temperature because even the solutions of stable xanthates of primary and secondary alcohols are decomposed at high temperatures (161). Freshly prepared solutions of pure xanthates are always used since their aqueous solutions are hydrolysed on standing (167). The presence of a little mineral acid which is essential for the ionisation of halogen cyanide, has an added advantage of minimising the possibility of hydrolysis of xanthates during the course of titration.

The visual determination of the xanthates with iodine cyanide is highly recommended for analytical purposes. The titrations are selective, reversible and as little as 1 mg in 50 ml solution is determined with ± 0.25 per cent error. Still better results are obtained if xanthates are treated with excess iodine cyanide or bromine cyanide which is then back titrated visually with ascorbic acid. It may be due to the fact that the decomposition of xanthates by an acid, if any, is minimised under these conditions because the reaction between the oxidant and the xanthate lasts for a shorter time.

Amperometric titrations

In the direct amperometric titrations of potassium n-propyl and allyl xanthates with iodine and bromine cyanides using a rotating platinum wire indicator electrode at a potential of
Oxidant/reductant (i-iv); Reductant/Oxidant (v-viii), molar ratio

Fig.11 - Direct (i-iv) and reverse (v-viii) amperometric titrations of potassium n-propyl xanthate (i, ii, v, vi) and potassium allyl xanthate (iii, iv, vii, viii) with iodine cyanide (i, iii, v, vii) and bromine cyanide (ii, iv, vi, viii) in aqueous medium
It is observed that the current is practically zero in the beginning and does not increase up to the equivalence point where it starts increasing gradually due to the cathodic reduction of the un consumed halogen cation resulting in a straight line plot (Fig. 11).

In the reverse titration of xanthates with bromine cyanide, the cathodic current due to the reduction of bromine cation decreases linearly as more and more of the reductant is added. After the equivalence point, the current remains constant. The shape of the reverse amperometric titration curves of these reductants with iodine cyanide is, however, different (Fig. 11) and is similar to one obtained in the corresponding titrations with metal ions (Fig. 3). The initial current which is due to the reduction of iodine cation, starts increasing instead of decreasing on adding the reductant until half of the theoretically required amount has been added. In these titrations, iodine cyanide is reduced to iodide which liberates iodine as a result of its reaction with unreacted oxidant imparting its colour to the solution. The gradual increase observed in intensity of the colour and the current is because of the formation of iodine which more than compensates the decrease in current due to corresponding consumption of iodine cyanide. However, the plot is not a straight line in more concentrated solutions but the half equivalence point is accurately located by extrapolation even in such cases. When iodine cyanide has been totally converted into iodine, the cathodic current decreases gradually.
Fig. 12 - Potentiometric titrations of (i) methyl xanthate, (ii) ethyl xanthate, (iii) n-propyl xanthate, (iv) iso-propyl xanthate, (v) allyl xanthate, (vi) n-butyl xanthate, (vii) iso-amyI xanthate, (viii) cyclohexanol xanthates (ix) benzyl xanthate with iodine cyanide in acetonitrile medium.
Potentiometric titrations of (i) methyl xanthate, (ii) ethyl xanthate, (iii) n-propyl xanthate, (iv) iso-propyl xanthate, (v) allyl xanthate, (vi) n-butyl xanthate, (vii) iso-amyl xanthate, and (viii) cyclohexanol xanthate with bromine cyanide in acetonitrile medium.
and linearly to zero value at the equivalence point and the solution becomes colourless, with further addition of the reductant, the current remains constant. However, the shapes of the direct and reverse bismarckian and bipotentiometric titration curves of potassium n-propyl xanthate with bromine cyanide and/or iodine cyanide (Fig. 8) are those which are commonly obtained for such systems.

Interferences

Carbon disulphide and alcohols which are the starting materials in the preparation of xanthates and may be present as impurities in certain samples, neither influence the stoichiometry of the reaction nor affect the accuracy of the titrations in aqueous medium. The decomposition products of xanthates such as thiosulphate, sulphite, sulphide and thiocarbonate, if present, react with these oxidants and thus interfere with the determination. However, if barium chloride solution (5 %) is added to the xanthate solution before performing the titrations, these ions are precipitated and the titrations proceed smoothly and quantitatively.

Titrations in nonaqueous solvents

The xanthates react in 2:1 molar ratio with iodine cyanide in acetonitrile, 1:1 ethanol - carbon tetrachloride mixture and ethyl acetate (Figs. 12, 14 and 16), and with bromine cyanide in acetonitrile and ethanol (Figs. 13 and 15). The best results are obtained in acetonitrile medium with both the oxidants (Tables X and XI). The error is less than ± 0.25 per cent, the change in potential at the equivalence point is fairly
Fig. 14 - Potentiometric titrations of (i) methyl xanthate, (ii) ethyl xanthate, (iii) n-propyl xanthate, (iv) iso-propyl xanthate, (v) allyl xanthate, (vi) n-butyl xanthate, (vii) t-butyl xanthate, (viii) iso-amyl xanthate, (ix) cyclohexanol xanthate, and (x) benzyl xanthate with iodine cyanide in 1:1 ethanol-carbon tetrachloride mixture.
Fig. 15 - Potentiometric titrations of (i) methyl xanthate, (ii) ethyl xanthate, (iii) n-propyl xanthate, (iv) iso-propyl xanthate, (v) allyl xanthate, (vi) n-butyl xanthate, (vii) t-butyl xanthate, (viii) amyl xanthate, (ix) cyclohexanol xanthate, (x) benzyl xanthate with bromine cyanide in ethanol medium
Fig. 16 - Potentiometric titrations of (i) methyl xanthate, (ii) ethyl xanthate, (iii) n-propyl xanthate, (iv) iso-propyl xanthate, (v) allyl xanthate, (vi) n-butyl xanthate, (vii) iso-amyl xanthate, (viii) cyclohexanol xanthate, (ix) benzyl xanthate with iodine cyanide in ethyl acetate.
large, and as little as 1 mg can be determined. However, potassium benzyl xanthate could not be titrated potentiometrically with bromine cyanide in this medium whereas the titration is successful in ethanol. Potassium t-butyl xanthate is insoluble in acetonitrile and ethyl acetate and thus cannot be determined. All the other titrations are quick, quantitative and easy to perform. The solution turns light yellow after the equivalence point. The titrations are carried out with iodine cyanide in these non-aqueous solvents, but no such colour change is observed in the titrations with bromine cyanide. The appearance of a yellow colour suggests that iodine cation is reduced to iodide when forms iodine with un consumed excess iodine cyanide.

The titration of xanthate with iodine cyanide in ethanol is not possible as the reaction is very slow and there is no sharp change in potential at the equivalence point. The addition of carbon tetrachloride, which is an inert solvent, enhances the potential change. The potentiometric titrations with bromine cyanide, on the other hand, are successful in ethanol even in the absence of carbon tetrachloride. The potential change is larger in this case than that in the corresponding titration with iodine cyanide. Since iodine is more electropositive than bromine, the covalent bond in case of iodine cyanide and ethanol is stronger and thus iodine cation is not so freely available for reaction with xanthates as is the bromine cation. The reaction in ethyl acetate medium is still slower. It is in keeping with its greater donor strength than ethanol.
Cambron and Whitby (163) have concluded from the qualitative studies that monosulphides are formed when bromine cyanide reacts with xanthates in alcoholic medium. Iodine cyanide is expected to behave similarly and the reaction in ethanol may, therefore, be represented by the following general equations:

\[
\begin{align*}
S & \rightarrow 2(\text{R}-\text{O} \equiv \text{S} \equiv \text{E}) + \text{XCN} \\
& \rightarrow (\text{R}-\text{O} \equiv \text{C} \equiv \text{S})_2 + \text{X} + \text{KCN}
\end{align*}
\]

Although dixanthogen is soluble in ethanol and acetonitrile, yet its solution could not be titrated with these oxidants indicating thereby that there is no reaction between them under the experimental conditions. Its presence as a reaction product, therefore, does not interfere with the titrations. The titrations are not possible in n-butanol which is a stronger donor solvent. Even the addition of carbon tetrachloride is of no advantage.

Xanthates are titrated potentiometrically in acetone medium with considerable success. But the reactions are relatively slow and the titrations are time consuming and are of no analytical interest. The determination is not possible in formamide which is still a stronger donor solvent. Berger (169) has determined xanthates with perchloric acid in glacial acetic acid. However, the results obtained during the present studies in this solvent, are not accurate because glacial acetic acid decomposes xanthates to liberate unstable xanthic acid. The addition of sodium acetate is of no use.
The use of nonaqueous solvents in the determination of xanthates is thus advantageous. It not only rules out the possibility of their decomposition by the acid but also provides a very simple method to be followed with excellent accuracy. The titrations with halogen cyanides in acetonitrile are particularly recommended for analytical purposes, keeping in view their accuracy, ease and change in potential at the equivalence point.

Conclusion

Thus methyl, ethyl, n-propyl, isopropyl, allyl, n-butyl, t-butyl, isoamyl, cyclohexyl and benzyl xanthates of potassium are determined with iodine and bromine cyanides in aqueous medium at pH 5.0 to 5.4 and in acetonitrile, ethanol, 1:1 ethanol - carbon tetrachloride mixture and ethyl acetate media visually and/or potentiometrically. The xanthates react in the molar ratio 2:1 with these oxidants and are oxidized to dixanthogen. The potentiometric titrations of bromine cyanide with xanthates, unlike with other reductants, are possible in aqueous medium even in absence of iodide which has to be added in visual titrations for nonavailability of some specific indicator. The titrations are quick, simple, accurate and reversible. As little as 1 mg is accurately determined in aqueous or acetonitrile medium.
The determination of dithiocarbamates has gained importance because of the wide applicability of these compounds as plant fungicides, accelerators in rubber industry and analytical reagents. Thorn and Ludwig (170) have critically reviewed the various methods employed for their determination in aqueous medium. The methods are laborious, time consuming, unreliable and have usually been investigated only for sodium diethyldithiocarbamate. No attempt has been made to generalise the method for alkyl and aryl substituted dithiocarbamates; all of which may not give quantitative results if the experimental conditions are kept the same as reported for sodium diethyldithiocarbamate. The titrations with heavy metal salts (170-172) are not satisfactory owing to the formation of basic salts and co-precipitation (159). Lambisan and Hair (173) have recently determined a few insoluble dithiocarbamates. Iodimetric method is, no doubt, rapid but Callan and Strafford's (174) method of iodimetric determination in alcoholic solution is not reliable as starch does not exhibit the usual colour change at the end point even on dilution with water. Linch (159) has modified it by titrating the alcoholic solution of dithiocarbamate using starch as an external indicator. But the end point is not easily detectable and the author has recommended it only as a rapid approximate method. No further work has been reported on the determination of these compounds in nonaqueous media. Electro-metric titrations have not been carried out with any oxidant in
Fig. 17 - Potentiometric titrations of (i) sodium methyldithiocarbamate, (ii) sodium dimethyldithiocarbamate, (iii) sodium ethyldithiocarbamate, (iv) sodium diethyldithiocarbamate, (v) sodium isopropyldithiocarbamate, (vi) sodium amylldithiocarbamate, (vii) ammonium phenyldithiocarbamate, (viii) sodium diphenyldithiocarbamate and sodium benzylidithiocarbamate with iodine cyanide in aqueous medium.
any medium and exact pH range even for visual iodimetric determinations has not been reported. Furthermore, bromo oxidants have not been employed for this purpose.

In the present studies, the determination of sodium methyl, sodium dimethyl, sodium ethyl, sodium diethyl, sodium isopropyl, sodium n-butyl, sodium amyl, ammonium phenyl, sodium diphenyl, and sodium benzyldithiocarbamates is carried out with iodine oyanide and bromine oyanide in aqueous and nonaqueous media. The results recorded in Tables XII—XV show that the oxidants react with various dithiocarbamates in the molar ratio 1:2 in aqueous medium. The mode of reaction may, therefore, be represented as given below:

\[
2 \text{R}_1\text{R}_2\text{SCS}_2^- + X^+ \rightarrow \text{R}_1\text{R}_2\text{SCS}^-\text{S}^-\text{CNR}_2\text{R}_1 + X^- 
\]

where \(\text{R}_1\) = alkyl or aryl group

and \(\text{R}_2\) = hydrogen, alkyl or aryl group

The reaction is quantitative with iodine oyanide and bromine oyanide in the pH range 2.1 to 2.6 and 2.2 to 6.7 respectively. The titrations with bromine oyanide are possible only in the presence of iodide. It has already been reported that thiuram disulphide is the oxidation product of dithiocarbamates with mild oxidising agents (170). In the present studies, the elemental analysis of the oxidation product which is insoluble in some cases, supports the formation of the corresponding thiuram disulphide during the titration.

The reaction of thiuram disulphide with iodine has been the main source of error in the iodimetric titrations of
- Potentiometric titrations of bromine cyanide with (i) sodium methylthiocarbamate, (ii) sodium dimethylthiodithiocarbamate, (iii) sodium ethylthiocarbamate, (iv) sodium isopropylthiocarbamate, (v) sodium allylthiocarbamate, (vi) sodium phenylthiocarbamate, (vii) sodium dibenzylthiocarbamate, (viii) sodium dibenzylthiourea, (ix) sodium dibenzylthiouronium bromide.
Dithiocarbamates (130,170). It hinders the development of blue colour with starch at the end point. Erratic results have, therefore, usually been obtained in iodimetric determinations. In the present investigation, the reaction of the oxident with thiuram disulphide has been avoided by extracting the oxidation product with petroleum ether, carbon tetrachloride or chloroform and delivering the oxident directly into the aqueous layer below the nonaqueous layer.

During these studies, it is observed that dimethyl-and diethyl-thiuram disulphides are soluble, and tetramethyl-, tetraethyl-, di-isopropyl-, dibutyl-, diphenyl- and dimethyl-thiuram disulphides are slightly soluble in water. Tetraphenyl- and dibenzyl-thiuram disulphides are insoluble in water, petroleum ether, carbon tetrachloride and chloroform. It is, therefore, possible to titrate diphenyl- and benzyl-dithiocarbamates even without adding petroleum ether. The titrations are quick, simple and reversible. Very accurate results are obtained and the error is less than ±0.25 per cent even with the solutions of low concentrations (≈ 0.0025N). As little as 1.5 mg of dithiocarbamate can be accurately determined in 25 ml solution.

Starch works quite satisfactorily as an indicator in the visual titrations of the dithiocarbamates with the halogen cyanides and a purple violet colour appears at the end point. However, in the reverse titrations, the blue colour appears on the very first addition of the reagent indicating, thereby, that the iodide formed reacts with iodine cyanide present in
excess yielding iodine. The colour goes on deepening as more and more of the reductant is added. When approximately half of the theoretically required amount has been added, the total iodine cyanide gets converted into iodine and the colour intensity does not increase any more on adding the reductant solution. In case of reverse titrations with bromine cyanide, the blue colour is quite deep right from the very beginning. The end point is marked by an abrupt disappearance of the colour in both the cases.

Effect of the acid concentration

The pH has a marked effect on these titrations. At very low acid concentrations, the halogen cyanides are not completely ionised which results in higher consumption of the oxidant. On the other hand, higher acid concentrations decompose dithiocarbamates yielding low results. It is, therefore, essential to maintain pH in the specific range. The acidic dithiocarbamate solution of the mentioned pH is titrated with standard sodium hydroxide solution and it has been found that the concentration of the acid used is too low to decompose the dithiocarbamate.

Interferences

All these titrations are successfully carried out in the presence of ammonium, sodium, zinc, barium, strontium and iron(II) ions suggesting that the dithiocarbamates of these cations can also be determined under these conditions. However, copper(II) interferes with the titrations because of its
Fig. 19 - Potentiometric titrations of (i) sodium methylthiocarbamate, (ii) sodium dimethylthiocarbamate, (iii) sodium ethylthiocarbamate, (iv) sodium diethylthiocarbamate, (v) sodium isopropylthiocarbamate, (vi) sodium amylthiocarbamate, (vii) ammonium phenylthiocarbamate, (viii) sodium diphenylthiocarbamate & (ix) sodium benzylthiocarbamate with iodine cyanide in ethanol.
Fig. 20 - Potentiometric titrations of (i) sodium methyl dithiocarbamate, (ii) sodium dimethyl dithiocarbamate, (iii) sodium ethyl dithiocarbamate, (iv) sodium diethyl dithiocarbamate, (v) sodium isopropyl dithiocarbamate, (vi) sodium amyl dithiocarbamate, (vii) ammonium phenyl dithiocarbamate, (viii) sodium diphenyl dithiocarbamate, and (ix) sodium benzyl dithiocarbamate with iodine cyanide in 1:1 ethanol-carbon tetrachloride mixture.
Reduction to copper(I) by cyanide (151) as well as iodide ions. Copper(I), thus formed, reacts with the oxidant.

Titrations in nonaqueous solvents

When a dithiocarbamate solution in ethanol, 1:1 ethanol-carbon tetrachloride mixture or acetone is titrated potentiometrically with iodine cyanide in the same solvent, the solution remains colourless in the beginning but turns yellow at the equivalence point and a change in potential occurs abruptly at the oxidant/reductant molar ratio of 1:2 (Figs. 19, 30 and 22). The appearance of the yellow colour at or just after the equivalence point indicates the formation of iodine subsequent upon the reaction of the iodine (formed during the titration) with one drop in excess of iodine cyanide. On further addition of the oxidant, the yellow colour deepens but the potential remains almost constant. The titrations in ethanol and acetone are slow and require considerable time. The addition of carbon tetrachloride to ethanol makes the titration faster but the change in potential at the equivalence point is lowered. Iodine cyanide behaves as a Lewis acid towards ethanol or acetone resulting in the weak bonding between I⁺ of iodine cyanide and oxygen of the donor solvent (84,85). The bonding in pure ethanol is stronger than that in ethanol-carbon tetrachloride mixture and thus its reaction with dithiocarbamates in the former case is slower than that in the latter. It is probably because of this fact that titrations may not be possible in stronger donor solvents such as formamide, dioxane and ethyl acetate.
Fig. 21 - Potentiometric titrations of sodium methyl dithiocarbamate (i, vi), sodium dimethyl dithiocarbamate (ii, vii), sodium ethyl dithiocarbamate (iii, viii), sodium diethyl dithiocarbamate (iv, ix) 
& sodium isopropyl dithiocarbamate (v, x) with bromine cyanide in ethanol (i-v) and acetonitrile (vi-x).
Fig. 22 - Potentiometric titrations of (i) sodium methylthiocarbamate, (ii) sodium dimethylthiocarbamate, (iii) sodium ethylthiocarbamate, (iv) sodium diethylthiocarbamate, (v) sodium isopropylthiocarbamate, (vi) sodium amyldithiocarbamate, (vii) ammonium phenylthiocarbamate, (viii) sodium diphenylthiocarbamate, (ix) sodium benzyldithiocarbamate with iodine cyanide in acetone.
The titrations are also unsuccessful in acidic solvents such as glacial acetic acid and 1:1 acetic acid - carbon tetrachloride mixture. Even the addition of anhydrous sodium acetate to glacial acetic acid is of no advantage.

The dithiocarbamates react with bromine cyanide in the molar ratio 2:1 in ethanol and acetonitrile media (Fig. 21, Table XV). The solution remains colourless and the oxidant is directly reduced to bromide. These titrations are, however, not possible in acetone medium.

The potentiometric titrations of the dithiocarbamates with both these oxidants in nonaqueous media are reversible, accurate (Tables XIV and XV) and change in potential at the equivalence point is fairly large in each case (Figs. 19-22).

Conclusion

It is thus evident from these studies that the determination of the dithiocarbamates with iodine cyanide and bromine cyanide in aqueous medium at pH 2.1 to 2.5 and 6.2 to 6.7 respectively is very accurate if the oxidation product is extracted with petroleum ether, carbon tetrachloride or chloroform. The reactions in nonaqueous media are similar, fast and quantitative. The use of nonaqueous solvents for these titrations is advantageous as the oxidation product need not be extracted.
**Determination of Thiourea and its Derivatives**

The methods of the determination of thiourea and its derivatives are based upon their desulphurisation, oxidation with various oxidants and complex formation with metal ions (130). Various attempts have been made to review the earlier work (130,175,176). Berka and Žýka (177,178) have determined thiourea and a few of its derivatives with bromate, iodate, periodate, chloramine T and bromosulphinic acid. Singh and co-workers (179) have also carried out redox determination of the thioureas in aqueous medium. The iodimetric method of Werner (180) is reported to be rapid and simple. Several modifications of this method have been suggested (181-183). However, the iodimetric determination of thiourea even in basic medium has got several limitations. The accuracy of the method depends upon various factors such as the order of mixing the reagents, duration of keeping the reaction mixture before titration and concentration of alkali and iodine (184). Čihalik and Šůvčka (185) have used potentiometric method of end point detection for its determination with iodine(I) chloride. No attempt has been made to determine thiourea and its derivatives iodimetrically in nonaqueous solvents.

**Determination with iodine cyanide in aqueous medium**

Iodine cyanide reacts with thiourea, ethylthiourea, isopropylthiourea, allylthiourea, acetylthiourea, α-phenylthiourea, benzylthiourea, o-tolylthiourea, benzoylthiourea, o-chlorophenylthiourea,
Fig. 23 - Potentiometric titrations of (i) thiourea, (ii) acetylthiourea, (iii) ethylthiourea, (iv) allylthiourea, (v) isopropylthiourea, (vi) α-phenylthiourea, (vii) α-chlorophenylthiourea, (viii) benzylthiourea, (ix) benzyolthiourea, (x) o-tolylthiourea, (xi) diphenylthiourea & (xii) α-benzoyl-β-phenylthiourea with iodine cyanide in sulphuric acid.
lhenylthiourea, and α'-benzoyl-β'-phenylthiourea quantitatively in the molar ratio 1:2 in the presence of hydrochloric or sulphuric acid and itself is reduced to iodide (Tables XVI and XVII, Figs. 23).

Different products have been obtained on oxidation of thiourea and its derivatives with different oxidants or with the same oxidant under different conditions (130, 176, 185, 186). Čihalik and Sucháčka (183) have reported the formation of formamidine disulphide on oxidation of thiourea with iodine(I) chloride in neutral to strongly acidic solutions. The reaction may, therefore, be represented by the following general equation:

\[
\begin{align*}
R_1H_3 & \quad 2C-SH + I^+ \\
R_2H & \quad \rightarrow C-S-S-C \quad + 2H^+ + I^- \\
\end{align*}
\]

where \(R_1\) and \(R_2\) are hydrogen, alkyl, aryl or acyl groups.

The oxidation of thiourea and its derivatives to disulphides suggests that in acidic medium, thiourea may be present in the form \(R_2NC\text{H}_2\text{HI}\), which is derived from its zwitter ion structure, \(R_2NC\text{H}_2\text{I}^+\). This is in agreement with its properties of being a neutral substance but behaving as a monobasic base forming stable salts with acids. A study of the dielectric constant of the solution of thiourea and some of its derivatives in water (137) and dioxane (188) have confirmed the existence of zwitter ion.

The titrations are carried out by taking both the components in the same mineral acid or thioureas in a dilute acid and iodine cyanide in glacial acetic acid. The reaction is dependent upon...
The acid concentration which needs to be adjusted carefully to a value given in Tables XVI and XVII. The titrations of only the alkyl thioureas are reversible. However, the reverse titrations are considerably slow and the disappearance of the blue colour cannot be detected as accurately as its appearance. Reaction indicators such as carbon tetrachloride, chloroform and benzene work successfully only in the titrations of thiourea and its alkyl derivatives. The method is, however, accurate.

When iodine cyanide is added to thiourea or its derivative, it is directly reduced to iodine. In slow reactions, the iodine cyanide has a tendency to react with the iodide forming iodine and thus tending to impart yellow colour to the solution. If the acid concentration is less, then the evolved iodine reacts even on slight shaking and the colour at once disappears. But when acid concentration is somewhat higher, the reaction of the temporarily formed iodine is expected to be slow and thus in the titrations of 1,3 disubstituted thioureas, the yellow colour appears even before the equivalence point and gradually changes to red. However, in the faster titrations, the solution becomes yellow only at or just after the equivalence point. These colour changes are easily detected during the potentiometric titrations. The appearance of yellow colour at equivalence point is well marked in faster titrations that alkyl thioureas can be easily titrated with iodine cyanide visually even without using an indicator but the titration should be carried out rather slowly near the end point.
Determination of bromine cyanide in aqueous medium

The direct titrations of the thioureas with bromine cyanide in the presence of potassium iodide and dilute mineral acid are not possible because the thioureas do not react quantitatively with the evolved iodine in acidic medium. The method is modified by first reacting acidic bromine cyanide with potassium iodide and then treating the liberated iodine with the thioureas in the presence of bicarbonate. Sufficient sodium bicarbonate is added to make the solution slightly basic. Thus only the water-soluble thioureas such as thiourea, ethylthiourea, isopropylthiourea, allylthiourea and acetylthiourea are determined. Bromine cyanide is not completely ionised under such conditions.

The usual method of preparing bromine cyanide from molecular halogen and alkali cyanide in alkaline medium ([83]) also indicates the stability of the molecular species in basic medium. However, the presence of the reductant consumes the liberated iodine and thus converts more and more of bromine cyanide to Br\(^+\). The unreacted bromine cyanide has, therefore, to be titrated with thiosulphate in acidic medium. The results obtained (Table XIX) indicate that the thioureas and bromine cyanide react together in the molar ratio 1:4 in the presence of sodium bicarbonate and the reaction may be explained as given below:

\[
\text{BrCN} + \text{H}^+ + 2\text{I}^- \rightleftharpoons \text{Br}^- + \text{CN}^- + \text{H}^+ + \text{I}_2
\]

\[
\text{RNH} = \text{CNHNH}_2 + 4\text{I}_2 + 10\text{NaHCO}_3 \rightarrow \text{RNH} = \text{CNHNH}_2 + \text{Na}_2\text{SO}_4 + 8\text{NaI} + 10\text{CO}_2 + 5\text{H}_2\text{O}
\]

where R = hydrogen, alkyl or acetyl group
Oxidant/reductant (I-III); Reductant/oxidant (IV-VI), molar ratio.

Fig. 24 – Direct (I-III) and reverse (IV-VI) amperometric titrations of thiourea (I,IV) and hydrazine sulphate (II,III,V,VI) with iodine cyanide (I,II,IV,V) and bromine cyanide (III,VI) in aqueous medium.
That the total sulphur is oxidised to sulphate has been confirmed by acidifying the contents at the end point with hydrochloric acid and precipitating it as barium sulphate in order to determine it by the usual method.

Bicarbonate should be free from any contamination of sodium carbonate and be added before the addition of thiourea because otherwise erratic results are obtained due to different modes of reaction in acidic and slightly basic media (130, 175).

Amperometric titration

The shape of the curves of direct and reverse amperometric titrations of thiourea with cyanide (Fig. 24) using a rotating platinum wire indicator electrode at a potential of +0.15V (vs SCE) is found to be similar to those obtained in the corresponding titrations of metal ions (Figs. 2 and 3) and xanthates (Fig. 11).

Interferences

It is found that acetic acid, succinic acid, oxalic acid, sodium formate, sodium acetate, potassium hydrogen phosphate and urea have no effect on the titrations. Nitric acid, mercury(II) and copper(II) salts, however, interfere with the titrations.

Determination in nonaqueous solvents

Thiourea and its derivatives are determined potentiometrically with iodine cyanide in glacial acetic acid, 1:1 acetic acid - acetic amylide mixture and methanol. They react with iodine cyanide in 2:1 molar ratio in a 1:1 mixture of acetic acid
Fig. 25 - Potentiometric titrations of (i) thiourea, (ii) acetylthiourea, (iii) ethylthiourea, (iv) allylthiourea, (v) isopropylthiourea, (vi) α-phenylthiourea, (vii) α-chlorophenylthiourea, (viii) benzylthiourea, (ix) o-tolylthiourea & (x) diphenylthiourea with iodine cyanide in glacial acetic acid
Fig. 26 - Potentiometric titrations of (i) thiourea, (ii) acetylthiourea, (iii) ethylthiourea, (iv) allylthiourea, (v) isopropylthiourea, (vi) α-phenylthiourea, (vii) α-chlorophenylthiourea, (viii) benzylthiourea, (ix) o-tolythiourea & (x) diphenylthiourea with iodine cyanide in glacial acetic acid-acetic anhydride mixture.
and acetic anhydride (Fig. 26), and the reactions may be explained as given above. An appreciable amount of heat is evolved during the titrations especially on the first additions of the oxidant. Iodine cyanide reacts with thiourea, ethylthiourea, isopropylthiourea and allylthiourea in 1:2 molar ratio. The yellow colour appearing on each addition of iodine cyanide disappears on shaking or standing for a while. The colour persists at the end point and its intensity increases gradually with further additions of the oxidant. However, iodine cyanide reacts with acetylthiourea, α-phenylthiourea, o-chlorophenylthiourea, benzylthiourea, o-tolythiourea and diphenylthiourea in 1:1 molar ratio in glacial acetic acid medium (Table XVIII; Fig. 25) and is thus reduced only to elementary iodine as is also evident from the fact that the solution starts acquiring yellowish tinge right from the beginning only in these titrations. The colour deepens on further additions of iodine cyanide.

The solutions in both the media are kept molar with respect to sodium acetate which should be perfectly anhydrous at least in glacial acetic acid medium. Even the traces of water result in greater consumption of iodine cyanide probably due to the hydrolysis of sodium acetate. The presence of higher concentrations of sodium acetate makes the titrations a bit faster but the increase in potential at the equivalence point decreases in magnitude. If sodium acetate is present in lesser amounts than the optimum one, the reaction becomes too slow.
Fig. 27 – Potentiometric titrations of (i) thiourea, (ii) ethylthiourea, (iii) allylthiourea, (iv) isopropylthiourea, (v) α-phenylthiourea, (vi) α-chlorophenylthiourea, (vii) benzylthiourea, (viii) o-tolylthiourea, (ix) diphenylthiourea & (x) α-benzoyl-β-phenylthiourea with iodine cyanide in methanol.
Fig. 28 - Potentiometric titrations of thiourea (i), ethylthiourea (ii), isopropylthiourea (iii), allylthiourea (iv), \( \alpha \)-phenylthiourea (v), benzylthiourea (vi) & o-tolylthiourea (vii) with bromine cyanide in methanol.
The observed potential change is in the range 30-50 mV. The titrations are reversible and relatively slow in the acetic acid - acetic anhydride mixture than in pure glacial acetic acid medium. The titrations of mono-substituted thioureas are faster than the corresponding titrations of disubstituted thioureas. The titrations of ethylthiourea and \( \alpha \)-phenylthiourea are faster than the rest. The reactions of benzoylthiourea and \( \alpha \)-benzoyl-\( \beta \)-phenylthiourea with iodine cyanide in these media are too slow to be followed even potentiometrically. The nature, the number and the position of the substituents all appear to influence the course of the reaction. In particular, the presence of acyl group is found to considerably reduce the speed of the reaction. However, bromine cyanide oxidises the thioureas in glacial acetic acid or 1:1 acetic acid - acetic anhydride mixture neither in the presence nor in the absence of anhydrous sodium acetate.

The colour changes and the stoichiometric ratios observed in the titrations of the thioureas with iodine cyanide in methanol medium are the same as those mentioned for the corresponding titrations in glacial acetic acid except that diphenylthiourea and \( \alpha \)-benzoyl-\( \beta \)-phenylthiourea react with iodine cyanide in 3:1 and 1:1 molar ratio respectively (Table XVIII; fig. 27). However, bromine cyanide reacts with the thioureas in the molar ratio 1:3 in this medium (Table XIX) and itself is reduced to bromide. The reactions of acetylthiourea and benzoylthiourea with both the oxidants in methanol are very slow and the titrations cannot be carried out. The titrations with iodine cyanide in methanol are slower than the corresponding titrations in glacial acetic acid and 1:1 acetic acid.
acid - acetic anhydride mixture but the potential changes at the equivalence point are relatively large (> 50 mV). The titrations of thioureas with halogen cyanides are possible only in slightly acidic media and all attempts to determine these compounds even in solvents such as acetone and ethyl acetate have failed.

Conclusion

It is evident from these studies that iodine cyanide reacts with various alkyl, aryl, acyl and 1,3 disubstituted thioureas in the molar ratio 1:2 in acidic aqueous medium whereas four molecules of bromine cyanide combine with one molecule of water soluble thioureas under the conditions studied. Iodine cyanide reacts with the thioureas in 1:2 molar ratio in 1:1 acetic acid - acetic anhydride mixture whereas it combines with alkythioureas in the molar ratio of 1:2 and with aryl thioureas in 1:1 molar ratio in glacial acetic acid and methanol. But diphenyl and α-benzoyl-β-phenylthioureas react with iodine cyanide in 2:1 and 1:1 molar ratio respectively in methanol. The titrations are possible with bromine cyanide only in methanol medium.

The solvent and the pH of the reacting solutions in aqueous medium have, therefore, a marked effect on the course of the reaction and the stoichiometry. The use of iodine cyanide in aqueous acidic medium is significant because iodine cannot be so successfully used under acidic conditions for the determination of the thioureas.
Determination of Hydrazine and its Derivatives

The ability of hydrazine to act as a reducing agent has been widely used as the basis for its determination. Browne and Shetterly (190) as well as Audrieth and Ogg (190) have critically reviewed the various methods employed and reported that the nature and proportion of the oxidation products are markedly influenced by the nature of the oxidizing agent, temperature, concentration of the reactants, the method adopted in bringing the substances together and the pH of the solution. The oxidation in acidic solutions even with moderate oxidizing agents has been found to be slow. However, hydrazine is appreciably oxidized even by air in basic medium, and nitrogen or carbon dioxide has to be passed over the solution during the titration. The determination of hydrazine with iodine in the presence of alkali and then back titrating the unconsumed iodine in acidic medium (191), suffers from several disadvantages including the decomposition of hydrazine by air. The number of oxidizing agents used is limited because it undergoes more than one reaction with several oxidants (192). Iodine (193-195), iodate (196,197) and bromate (198,199) have usually been employed for the purpose. Berka and Zyka (200) have successfully used chloramine T, ferri cyanide, lead(IV) and periodate. An attempt has been made to determine hydrazine and its derivatives with pseudohalogen and with any oxidant in nonaqueous media.

In the present studies, it is observed that iodine cyanide and bromine cyanide react quantitatively in aqueous medium at pH 4.6 to 5.0 and 4.8 to 5.3 respectively with chloramine
Fig. 29 - Potentiometric titrations of (i) hydrazine sulphate, (ii) acetylhydrazine, (iii) chloralhydrazine, (iv) 1,1 dimethylhydrazine hydrochloride, (v) 1,1 diethylhydrazine hydrochloride, (vi) phenylhydrazine hydrochloride, (vii) benzalazine, (viii) hydroxylamine hydrochloride, (ix) benzylhydrazine hydrochloride, (x) p-tolylhydrazine hydrochloride & (xi) 1,1 methyl phenylhydrazine with iodine cyanide in aqueous medium.
and water soluble salts of hydrazine, phenylhydrazine and benzyl-
hydroxylamine in the molar ratio 2:1 and with acetylhydrazine and 
1,1 diethylphenylhydrazine and salts of 1,1 dimethylhydrazine, 
1,1 diethylhydrazine and p-tolylhydrazine in 1:1 molar ratio
(Figs. 29 and 30). However, two equivalents of hydrazylamine 
hydrochloride react with one equivalent of iodine cyanide and 
borine cyanide at pH 3.6 to 4.0 and 6.7 to 7.2 respectively.
Benzalalazine does not consume bromine cyanide whereas it reacts 
with iodine cyanide at pH 2.7 to 3.2 in the molar ratio 1:2
(Table XX). The nature, the number and the position (whether 
symmetrically or unsymmetrically placed) of the substituents 
all seem to exert a marked influence on the stoichiometry.
Although the titrations of hydrazines with bromine cyanide are 
carried out in the presence of iodide, yet the role of Br⁺ in 
these titrations is evident from the fact that hydrazine and its 
derivatives are titrated with bromine cyanide quantitatively below 
pH 5.3 whereas the titrations with iodine have been successfully 
carried out only in basic medium (120).

Hydrazine and its derivatives are oxidised by weak oxidising 
agents in aqueous medium to nitrogen or substituted tetrazene 
(128,130,190). The reactions with iodine cyanide and bromine cyanide
(XCl) may, therefore, be explained as below:

\[
\begin{align*}
\text{H}_2\text{H}_4 + 2 X^- & \rightarrow \text{N}_2 + 4 \text{H}^+ + 2 X^- \\
\text{R}_1\text{H}_{2}\text{N} + 2 X^- & \rightarrow \text{R}_1\text{X} + \text{N}_2 + 3 \text{H}^+ + X^- \\
\end{align*}
\]

where \( \text{R}_1 = \text{C}_6\text{H}_5^- \) or \( \text{C}_6\text{H}_5\text{CH}_2^- \).
\[ \text{CCL}_3\text{CH(ONH)}_2 + 2 X^+ \rightarrow \text{CCL}_3\text{CHO} + N_2 + 4 H^+ + 2 X^- \]
\[ 2 \text{CH}_2\text{CONH}_2 + 2 X^+ \rightarrow \text{CH}_2\text{CONH}_2\text{COCH}_3 + N_2 + 4 H^+ + 2 X^- \]
\[ 2 \text{NH}_2 + 2 X^+ \rightarrow \text{NN} \equiv \text{NN} \ + 4 H^+ + 2 X^- \]

where \( R_2 = \) hydrogen or alkyl group

and \( R_3 = \) alkyl or aryl group

\[ 2 \text{NH}_2 \text{OH} + X^+ \rightarrow N_2 + 2 H_2O + 2 H^+ + X^- \]
\[ \text{C}_6\text{H}_5\text{CNHCHC}_6\text{H}_5 + 2 I^- + 2 H_2O \rightarrow 2 \text{C}_6\text{H}_5\text{CHC} + N_2 + 4 H^+ + 2 I^- \]

The evolution of nitrogen gas in the above titrations is observed by collecting it in a closed system using an air thermostated graduated pipette connected to a small water reservoir.

The pH is maintained in the specific range by adding sodium bicarbonate solution, whenever necessary. Sodium bicarbonate, if present alone or in excess, decomposes the hydrazines (194). The use of iodine cyanide or bromine cyanide for these determinations has, therefore, a marked advantage over the other oxidants because these react below \( pH \) 5.3 avoiding all chances of air oxidation and decomposition of hydrazines due to the presence of bicarbonate. The titrations are very simple to perform and reversible.

The reactions are too slow to be followed titrimetrically when acetate buffer of \( pH \) 4.5 is used in place of bicarbonate in
Fig. 30—Potentiometric titrations of (i) hydrazine sulphate, (ii) acetylhydrazine, (iii) chloralhydrazine, (iv) dimethylhydrazine hydrochloride, (v) 1,1 diethylhydrazine hydrochloride, (vi) hydroxylamine hydrochloride, (vii) benzylhydrazine hydrochloride, (viii) p-tolylhydrazine hydrochloride, (ix) phenylhydrazine hydrochloride & (x) 1,1 methylphenylhydrazine with bromine cyanide in aqueous medium.
these titrations. However, the results obtained are satisfactory if excess of halogen cyanide added to the hydrazine solution containing acetate buffer, is titrated with thiosulphate after allowing it to stand for about 30 minutes.

The reaction between hydrazines and iodine cyanide or bromine cyanide at higher acid concentrations is extremely slow and far from being quantitative. Hydrazine has been determined with iodine in concentrated sulphuric acid medium (201) but the titration could not be repeated and erratic results are obtained due to the reasons stated above.

**Indicators**

Starch, carbon tetrachloride and chloroform have been employed as indicators. However, the end point is well marked in the absence of indicators by the abrupt appearance of a yellow colour at the end point due to the presence of free iodine. The yellow colour should persist for a few minutes. It is significant because the reaction of iodine with hydrazines in the presence of starch is slow, particularly near the end point (194). The bromine cyanide titrations are slower than the corresponding iodine cyanide titrations when starch is used as an indicator. The last additions of the oxidant are, therefore, made slowly and dropwise.

**Potentiometric titrations**

All the titrations are successfully carried out potentiometrically under similar conditions. The potential increases rapidly at the equivalence point and then gradually returns to a new and different constant value. These titrations are slow
but accurate (Tables XX and XXI) and the change in potential at the equivalence point is fairly large in each case (Figs. 29 and 30).

Amperometric titrations of hydrazine sulphate

Direct and reverse amperometric titrations of hydrazine sulphate with iodine cyanide and bromine cyanide at pH 4.6 to 5.0 and 4.8 to 5.3 respectively are carried out in an inert atmosphere with a rotating platinum wire indicator electrode at a potential of +0.15 V (vs SCE). The shapes of the curves (Fig. 24) are similar to those obtained in the corresponding titrations of metal ions (Figs. 2 and 3) and xanthates (Fig. 11) with these oxidants.

Interferences

The determination of hydrazine and its derivatives in the presence of ammonia is of interest, not only because it may be present as an impurity in hydrazine but also as it is formed in many of its redox reactions. Ammonia has been reported to interfere in the determination of hydrazine with iodine in alkaline medium (203). However, the presence of ammonium salts is found to have no effect on the titrations in the present studies. Chloramine which is one of the intermediate products in the preparation of dialkylhydrazines, interferes with the titrations and amount of the oxidant consumed is lesser than that theoretically required, because it oxidises the iodide formed back to iodine. A precipitate is formed on adding iron(III) salts to the reductant solution and the amount of halogen cyanide consumed is lesser than that required stoichiometrically. However, it is
Fig. 31 - Potentiometric titrations of hydrazine hydrate (v, vii), chloralhydrazine (iii, vii), phenylhydrazine (ii, viii), methylphenylhydrazine (i, ix), & ben zalazine (iv, x) with iodine cyanide in glacial acetic acid (i-v) and 1:1 acetic acid - acetic anhydride (vi-x).
Fig. 32- Potentiometric titrations of hydrazine hydrate (i, iv), phenylhydrazine (ii, vi), methyphenylhydrazine (iii, vii) & chloralhyrazine (iv, viii) with bromine cyanide in glacial acetic acid (i-iv) and 1:1 acetic acid - acetic anhydride (v-viii)
not unexpected as iron(III) compounds have been employed as oxidants for the determination of hydrazine (203). The addition of pyrophosphate makes the presence of iron(III) ineffective and the titration proceeds smoothly.

Titrations in nonaqueous media

Phenylhydrazine, chloralhydrazine and 1,1 methylphenylhydrazine react with iodine cyanide and bromine cyanide in 1:1 molar ratio in glacial acetic acid and in 2:1 molar ratio in 1:1 acetic acid - acetic anhydride mixture media (Figs. 31 and 32). Hydrazine hydrate consumes equimolar quantities of the oxidant in both the media. Benzalazine reacts with iodine cyanide in 1:1 and 2:1 molar ratios in glacial acetic acid and 1:1 acetic acid - acetic anhydride mixture respectively. However, it is not oxidised by bromine cyanide in these media. The reactions are quantitative only when the solutions are molar with respect to sodium acetate (Tables XXII and XXIII). Certain other substituted hydrazine salts could not be determined because of their insolubility in glacial acetic acid and acetic anhydride. In the titrations with iodine cyanide, the solutions acquire a yellow colour near the equivalence point and then gradually become yellowish brown. In nonaqueous media, the stoichiometric ratios are different from those obtained in aqueous medium except for the reaction of methylphenylhydrazine. The reactions in glacial acetic acid may be explained by the following equations:
The reactions in 1:1 acetic acid-acetic anhydride mixture are exothermic. The mode of reaction is expected to be different due to the presence of acetic anhydride which reacts with these hyrazines as given below (204, 205):

\[ \text{NH}_2\text{NH}_2 + (\text{CH}_3\text{CO})_2\text{O} \rightarrow \text{CH}_3\text{CONH}_2 + \text{CH}_3\text{COOH} \]

\[ \text{C}_6\text{H}_5\text{NNH}_2 + 2 (\text{CH}_3\text{CO})_2\text{O} \rightarrow \text{N} = \text{N} + 2 \text{CH}_3\text{COOH} \]

\[ \text{C}_6\text{H}_5\text{NNH}_2 + 2 (\text{CH}_3\text{CO})_2\text{O} \rightarrow \text{CH}_3\text{CONH}_2 + \text{CH}_3\text{COOH} \]

\[ \text{CCl}_3\text{CH(OH)}\text{NNH}_2 + 2 (\text{CH}_3\text{CO})_2\text{O} \rightarrow \text{CCl}_3\text{CH(OH)}\text{CONH}_2 + 2 \text{CH}_3\text{COOH} \]

By analogy with the reactions explained earlier, the oxidation of these acetyl derivatives with the halogen cyanide may be represented as below:
It seems difficult to explain the mode of reaction of benzanilide with iodine cyanide in nonaqueous solvents.

The change in potential in glacial acetic acid medium is larger than that in 1:1 acetic acid + acetic anhydride mixture which in turn is appreciably larger than that in aqueous medium. Very accurate results are obtained particularly in glacial acetic acid medium. The addition of sodium acetate which is a strong base in these solvents, is necessary as it adjusts the pH of the solution due to its buffering action. Since the medium is distinctly acidic, there are no chances of air-oxidation of the hydrazines.

Conclusion

Thus iodine cyanide and bromine cyanide react quantitatively at pH 4.6 to 5.0 and 4.8 to 5.3 respectively with chloral hydrazine and water soluble salts of hydrazines, phenylhydrazines and benzylhydrazines in the molar ratio 2:1, and with acetylhydrazine, 1,1-methylphenylhydrazine and acid salts of 1,1-dimethyl-, 1,1-diethyl- and p-tolyl-hydrazines in the molar ratio 1:1. Hydroxylamine reacts
With these oxidants in the molar ratio 2:1 at pH 3.6 to 4.0 and 6.7 to 7.2 respectively. The hydrazines are oxidized to nitrogen or substituted tetrazenes. Hydrazine hydrate, phenylhydrazine, chloralhydrazine, 1,1 methylphenylhydrazine and benzalazine are determined with bromine cyanide and/or iodine cyanide potentiometrically in glacial acetic acid and 1:1 acetic acid - acetic anhydride mixture, keeping the solutions molar with respect to sodium acetate. These hydrazines react in the molar ratios 1:1 in the former and 2:1 in the latter media except for hydrazine hydrate which consumes equimolar quantities of the oxidant in both the media. The mode and progress of the reaction are largely influenced by the nature of the solvent and the oxidizing agent. The titrations are simple, accurate and reversible.
The oxidation and substitution reactions of phenols with halogens, hypohalites and iodine(I) chloride have been critically reviewed by Koltchoff and Belcher (128) as well as by Ashworth (130). Iodine (130, 206) and iodine(I) chloride (130) are known to oxidise polyphenols to quinones in aqueous medium. Komárek and Valcha (207) have titrated hydroquinone and resorcinol with iodine(I) chloride potentiometrically. Phenol, o-cresol and resorcinol have been reported to form tribromo derivatives with bromine and hypobromites (130) whereas thymol yields a dibromo derivative with bromine (128). Day and Taggart (208) have reported the quantitative formation of tribromo derivative on the reaction of phloroglucinol with excess of bromine. Šíhalík and Vavrajsova (209) have titrated hydroquinone and metol with iodine(I) chloride both in acidic and basic media. Berka and Sýka (210) have carried out the oxidation of hydroquinone to quinone with dibromomuconimide.

In the present investigations, the reactions of phenol, o-cresol, m-cresol, p-cresol, o-ethylphenol, p-ethylphenol, thymol, eugenol, hydroquinone, resorcinol, phloroglucinol and 3-naphthol with iodine cyanide and bromine cyanide are studied in different media with a view to understanding the mode of reaction as well as the effect of pH, time and temperature.

The experimental conditions for stoichiometric reactions and the results thus obtained in aqueous medium are summarised in Tables A and B.
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<th>Temperature °C</th>
<th>Time hour</th>
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<td></td>
<td>4</td>
<td>25-30</td>
<td>72</td>
<td>1:1</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>50-60</td>
<td>1</td>
<td>2:1</td>
</tr>
</tbody>
</table>
Phloroglucinol  & 68-73 & 1 & 2:1  
& 68-73 & 1 & 2:1  
& 68-73 & 1 & 1:1  

& 4 88-88  & 0.75 & 2:1  
& 62-63 & 1 & 1:1  

It is evident, therefore, that phenol, cresols and ethylphenols are brominated to their tribromo derivatives with almost similar ease.

$$\text{RC}_6\text{H}_4\text{OH} + 3 \text{Br}^+ \rightarrow \text{RC}_6\text{H}_4\text{OKBr}_3 + 3 \text{H}^+$$

where $R = \text{H}$ or $\text{CH}_3$, $\text{C}_2\text{H}_5$.

Phloroglucinol undergoes a stepwise bromination up to tribromo-phloroglucinol. It may be mentioned that Kolthoff and Bolzher (128) have remarked that the cresols are not brominated so readily as the other phenols and that the phenols having alkyl group in the para position, do not undergo quantitative substitution with bromine. The reaction has been inferred to be very complex involving oxidation, addition as well as substitution (128). Furthermore, m-cresol is reported to be easily brominated than o- and p-cresols (211).

In the present studies, the substitution is found to be a function of acid concentration, time and temperature of refluxing. The degree of bromination increases with the increase in these factors and a careful control of the experimental conditions is essential to obtain reproducible results. The reactions are
not stoichiometric under the conditions other than those mentioned in Table A. At lower temperature or acid concentration, only monosubstituted products are formed except in case of o-cresol where disubstitution occurs.

\[
\text{RC}_6\text{H}_4\text{OH} + \text{Br}^+ \rightarrow \text{RC}_6\text{H}_4\text{OBr} + \text{H}^+
\]

Disubstitution in o-cresol is in keeping with the work of Richenegg and Haynes (212). The bromination of phenol to bromophenol could not be achieved even by varying the experimental conditions.

Sprung (213) believes that bromination occurs in alkyl group ortho or para to phenolic hydroxy group. Ruderman (214) has suggested as an alternative explanation that methylquinones are formed and consume additional bromine. No direct evidence is available to support either theory (128). Veubel (215) has suggested that the bromine always takes position which is ortho or para to hydroxyl group. None of the ordinary substituents like methyl or halogen, when present in positions ortho and para to hydroxyl group, hinder the entrance of bromine into the other ortho and para positions.

The behaviour of certain phenols towards iodine cyanide is, however, different (Table B).
### Table B - Reaction of iodine cyanide with phenols

<table>
<thead>
<tr>
<th>Phenol</th>
<th>Acid molarity M</th>
<th>Temperature °C</th>
<th>Time hour</th>
<th>ICl/Phenol molar ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol</td>
<td>4</td>
<td>70-80</td>
<td>1</td>
<td>1:1</td>
</tr>
<tr>
<td>o-Cresol</td>
<td>4</td>
<td>55-60</td>
<td>1</td>
<td>2:1</td>
</tr>
<tr>
<td>p-Cresol</td>
<td>4</td>
<td>60-70</td>
<td>1</td>
<td>1:1</td>
</tr>
<tr>
<td>p-Hexylphenol</td>
<td>6</td>
<td>60-70</td>
<td>1</td>
<td>1:1</td>
</tr>
<tr>
<td>Thymol</td>
<td>6</td>
<td>60-70</td>
<td>1</td>
<td>2:1</td>
</tr>
<tr>
<td>Catechol</td>
<td>4</td>
<td>60-70</td>
<td>3</td>
<td>1:1</td>
</tr>
<tr>
<td>Resorcinol</td>
<td>4</td>
<td>25-30</td>
<td>12</td>
<td>2:1</td>
</tr>
<tr>
<td>Hydroquinone</td>
<td>4</td>
<td>80-60</td>
<td>0.5</td>
<td>2:1</td>
</tr>
<tr>
<td>Phloroglucinol</td>
<td>4</td>
<td>50-60</td>
<td>1</td>
<td>1:1</td>
</tr>
<tr>
<td>o-Naphthol</td>
<td>4</td>
<td>55-60</td>
<td>1</td>
<td>1:1</td>
</tr>
</tbody>
</table>
Fig. 33 - Potentiometric titrations of phenol (i), o-cresol (ii), m-cresol (iii), p-cresol (iv), o-ethylphenol (v), p-ethylphenol (vi), thymol (vii), catechol (viii), resorcinol (ix), hydroquinone (x), phloroglucinol (xi) & β-naphthol (xii) with iodine cyanide in glacial acetic acid.
Fig. 34 - Potentiometric titrations of phenol (i), o-cresol (ii), m-cresol (iii), p-cresol (iv), o-ethylphenol (v), p-ethylphenol (vi), thymol (vii), catechol (viii), resorcinol (ix), hydroquinone (x), phloroglucinol (xi) & β-naphthol (xii) with iodine cyanide in 1:1 acetic acid - acetic anhydride.
Phenol, cresols, ethylphenols, phloroglucinol and \( \beta \)-naphthol do not undergo trisubstitution. The reaction leading to monosubstitution, as exemplified by o-cresol, may be explained as below:

\[
\text{CH}_3\text{C}_6\text{H}_4\text{OH} + \text{I}^- \rightarrow \left( \begin{array}{c} \text{CH}_3 \\ \text{I} \\
\end{array} \right) \rightarrow \text{CH}_3\text{C}_6\text{H}_4\text{I}^{-}
\]

Di-iodination is also noted in case of o-cresol, m-cresol and phloroglucinol whereas thymol undergoes disubstitution both with iodine cyanide and bromine cyanide in aqueous medium. Stoichiometric results cannot be obtained for mono- or trisubstitution in case of thymol even by varying the factors considerably.

Hydroquinone, resorcinol and catechol react with halogen cyanides in the molar ratios 1:1 and 1:2 indicating, thereby, the possibility of monosubstitution:

\[
\begin{align*}
\text{HOC}_6\text{H}_4\text{OH} + \text{I}^- & \rightarrow \text{HOC}_6\text{H}_3\text{I}^- + \text{H}^+ \\
\text{HOC}_6\text{H}_3\text{OH} + \text{I}^- & \rightarrow \text{HOC}_6\text{H}_2\text{I}^- + \text{H}^+
\end{align*}
\]

The reaction of dihydroxyphenols with iodine(1) chloride in acidic aqueous medium in the molar ratio 1:2 has, however, been attributed to their oxidation to quinones (130).

Reactions in Nonaqueous Solvents

Phenol, alkylphenols and \( \beta \)-naphthol react with iodine cyanide and bromine cyanide in the molar ratio 1:1 in glacial acetic acid and 1:1 acetic acid - acetic anhydride mixture and the reaction may be attributed to monosubstitution. However, a step-wise 1- and
Fig. 35- Potentiometric titrations of phenol (i), o-cresol (ii), m-cresol (iii), p-cresol (iv), o-ethylphenol (v), p-ethylphenol (vi), thymol (vii), catechol (viii), resorcinol (ix), hydroquinone (x), & phloroglucinol (xi) with bromine cyanide in glacial acetic acid.
Fig. 36 - Potentiometric titrations of phenol (i), o-cresol (ii), m-cresol (iii), p-cresol (iv), o-ethylphenol (v), p-ethylphenol (vi), thymol (vii), catechol (viii), resorcinol (ix), hydroquinone (x), phloroglucinol (xi) & β-naphthol (xii) with bromine cyanide in 1:1 acetic acid - acetic anhydride
tri-substitution is also observed during the reaction of phenol, o-cresol, o-ethylphenol and p-ethylphenol with bromine cyanide, whereas phloroglucinol reacts with both the halogen cyanides in both the media in the molar ratios 1:1, 1:2 and 1:3. The reaction of o-cresol and thymol with iodine cyanide in these media results in the formation of only a monosubstituted product whereas disubstituted products are also obtained in case of its reaction with bromine cyanide. n-Naphthol does not react with bromine cyanide in glacial acetic acid medium unlike that in a 1:1 mixture of glacial acetic acid and acetic anhydride. Similarly p-cresol undergoes mono- and disubstitution with bromine cyanide in the mixture medium whereas only mono-bromoderivative is obtained in glacial acetic acid. The reactions may be explained by the following general equations:

$$\text{PhOH} + \text{I}^+ \rightarrow \text{PhI} + \text{H}^+$$

$$\text{PhOH} + \text{Br}^+ \rightarrow \text{PhBr} + \text{H}^+$$

Monoresol, catechol and hydroquinone react with iodine and bromine cyanides in the molar ratio 1:2 in both these nonaqueous media.

Conclusion

It is evident from these studies that bromination is easier than iodination. The overall effectiveness of these reagents in aromatic substitution is iodine cyanide < bromine cyanide. The reaction is dependent upon the nature of phenol, halo cyanide and the solvent. Since the phenols undergo electrophilic substitution, these reactions are thus not due to the oxidizing behaviour of the halogen cyanides. It is, however, reasonable that I^+ and Br^+ are the electrophiles in these substitution reactions.