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Estimation of Hydrazine and its Derivatives with Iodine cyanide and Bromine cyanide

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Iodine cyanide and bromine cyanide react quantitatively at *p*H 4.6--5.0 and 4.8--5.3 respectively with water soluble salts of hydrazine, phenylhydrazine, benzylhydrazine and chloral hydrazine 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 *p*H 3.6--4.0 and 6.7--7.2 respectively. The hydrazines are oxidised to nitrogen or substituted tetrazenes. Hydrazine hydrate, phenylhydrazine, chloralhydrazine, 1 : 1 methylphenylhydrazine and benzalazine have been estimated with iodine cyanide potentiometrically in glacial acetic acid and 1 : 1 acetic acid-acetic anhydride mixture, keeping 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 only one equivalent of the oxidant in both the media. The titrations are simple, accurate and reversible.

The ability of hydrazine to act as a powerful reducing agent has been widely used as the basis for its estimation. Browne and Shetterly[1] as well as Audrieth and Ogg[2] 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 oxidising agent, temperature, concentration of the reactants, the method adopted in bringing the substances together and the *p*H of the solution. The oxidation in acidic solutions even with moderate oxidising agents has been found to be slow. However, it is appreciably oxidised by air in basic medium and nitrogen or carbon dioxide has to be passed over the solution during the titration[2]. The estimation of hydrazine with iodine in the presence of alkali and then back titrating the unconsumed iodine in acidic medium, suffers from several disadvantages including decomposition of hydrazine by air and alkali[3]. The number of oxidising agents used is limited because it undergoes more than one reaction with several oxidants[4]. Iodine[5–7], iodate[8,9] and bromate[10,11] have usually been employed for the purpose. No attempt has been made to estimate hydrazine and its derivatives with interhalogens or pseudohalogens in aqueous medium and with any oxidant in non-aqueous medium. Recently, iodine cyanide[12,13] and bromine cyanide[13,14] have been developed as volumetric oxidants for the estimation of metal ions and dithiocarbamates in these laboratories. In the present investigations, these compounds have been used for the determination of hydrazine and its organic derivatives in aqueous as well as non-aqueous media to study the effect of the oxidant, the degree and kind of the substitution in the reductant and the solvent on the mode of reaction.

EXPRIMENTAL

Materials : Iodine cyanide, bromine cyanide[14], acetylhydrazine[15], chloralhydrazine[16], 1 : 1 dialkylhydrazine hydrochloride[17], 1 : 1 methylphenylhydrazine, benzalazine[18], benzylhydrazine hydrochloride[19] and *p*-tolylhydrazine hydrochloride[20] were prepared and purified according to the procedures reported in the literature. Hydrazine sulphate (E.Merck), phenylhydrazine hydrochloride (Johnson, England) and hydroxylamine hydrochloride (Rudy Pont, Germany) were crystallised from hot water. Phenylhydrazine (Riedel, Germany) was distilled twice at 243°/760 mm. Hydrazine hydrate (80%, Riedel, Germany), was used as such.

Solutions : Iodine cyanide solutions (0·025 *M*) were prepared in 0·1 *M* sulphuric acid, 0·1 *M* hydrochloric acid, glacial acetic acid and 1 : 1 acetic acid-acetic anhydride mixture. Bromine cyanide solution (0·025 *M*) was prepared in 0·1 *M* hydrochloric and sulphuric acids. The solutions of hydrazine and its derivatives (0·025 *M*) were prepared in distilled water, glacial acetic acid and 1 : 1 acetic acid-acetic anhydride mixture by direct weighing. But the aqueous solutions of 1 : 1 methylphenylhydrazine and benzalazine were prepared by dissolving in ethanol (one part) and diluting with water (24 and 3 parts respectively). The solutions of the reductants were standardised according to the reported methods[2].

Visual titrations in aqueous medium : An aliquot of each reductant solution (5–25 ml) taken in a titration cell was diluted with water (10–50 ml). Potassium iodide (0·5–1 g.) was added in the titrations with bromine cyanide. The electrodes of the *p*H meter were dipped in the solution. It was titrated with standard solutions of iodine cyanide or bromine cyanide adjusting the *p*H with one per cent sodium bicarbonate solution in the ranges 4·6–5·0 and 4·8–5·3 for all the reductants except for hydroxylamine hydrochloride which was titrated with these oxidants at *p*H 3·6–4·0 and 6·7–7·2 respectively. Aqueous starch solution (0·5 ml, 1%) was added near the end point which was marked by the appearance of a permanent blue colour. Chloroform and carbon tetrachloride (1–2 ml) were also employed as extraction indicators which turned pink at the end point.

Potentiometric titrations in aqueous medium : An aliquot of each reductant solution (5–25 ml) taken in a 100 ml titration cell was diluted to 50–70 ml with water and titrated with the oxidant under the conditions mentioned for visual titrations using the potentiometric titration outfit described earlier[12]. After each addition of the oxidant, the contents were thoroughly stirred and the potential noted. The e.m.f. was plotted as a function of oxidant/reductant molar ratio.

Potentiometric titrations in non-aqueous media : An aliquot of each reductant solution (5–25 ml) in glacial acetic acid or 1 : 1 acetic acid-acetic anhydride mixture was diluted to 50–70 ml with the same solvent. Anhydrous sodium acetate (5–7 g) was added and the contents were titrated with iodine cyanide.

Some typical results of these estimations have been presented in Tables 1–2 and Figs. 1–4.

TABLE 1

Visual and potentiometric estimations of hydrazine and its derivatives with Iodine cyanide and Bromine cyanide in aqueous medium

Reductant	Iodine cyanide Amount of reductant, mg.				Bromine cyanide Amount of reductant, mg.			
	Taken	Found	Taken	Found	Taken	Found	Taken	Found
	(Visual method)		(Potentiometric method)		(Visual method)		(Potentiometric method)	
Hydrazine sulphate	53.25	53.25	66.64	66.75	56.00	56.12	70.00	70.11
	35.50	35.59	53.51	53.21	44.80	44.70	42.00	41.90
	17.75	17.72	33.32	33.40	28.00	27.95	28.00	27.95
Acetylhydrazine	46.25	46.17	46.50	46.44	46.25	46.36	46.25	46.33
	37.00	37.05	37.00	36.88	37.00	37.15	27.75	27.82
	18.50	18.53	18.50	18.46	18.50	18.56	18.50	18.45
Chloralhydrazine	44.68	44.63	111.48	111.65	89.36	89.55	111.70	111.95
	38.74	38.81	89.18	89.38	71.48	71.39	67.02	67.19
	22.34	22.38	55.74	55.94	44.68	44.80	44.68	44.77
1 : 1 Dimethylhydrazine	50.56	50.67	50.56	50.47	62.50	62.44	78.12	78.00
hydrochloride	40.45	40.58	40.45	40.54	50.00	50.20	46.87	46.75
	25.28	25.38	25.28	25.34	31.25	31.17	31.25	31.33
1 : 1 Diethylhydrazine	50.67	50.57	50.67	50.74	84.42	84.22	105.52	105.74
hydrochloride	40.54	40.45	40.54	40.44	67.53	67.38	63.31	63.14
	25.34	25.23	25.34	25.28	42.21	42.09	42.21	42.10
1 : 1 Methylphenyl	62.80	62.94	62.80	62.94	62.80	62.92	78.50	78.40
hydrazine	50.14	50.02	50.14	50.05	50.14	50.28	47.10	47.19
	31.40	31.48	31.40	31.47	31.40	31.32	31.42	31.47
Phenylhydrazine	80.80	81.00	53.80	53.90	53.80	53.71	67.25	67.10
hydrochloride	64.64	64.52	42.04	41.93	42.04	42.13	40.35	40.38
	40.40	40.29	26.90	26.96	26.90	26.98	26.90	26.82
Benzylhydrazine	42.20	42.13	42.20	42.31	84.40	84.50	105.50	105.68
hydrochloride	33.76	33.84	33.76	33.85	67.52	67.65	63.30	63.44
	21.10	21.16	21.10	21.07	42.20	42.29	42.20	42.30
p-Tolylhydrazine	106.40	106.60	91.68	91.53	106.40	106.17	133.00	133.19
hydrochloride	85.12	85.31	73.34	73.20	85.12	85.30	79.80	79.95
	53.20	53.33	45.84	45.72	53.20	53.31	53.20	53.32
Benzalazine	105.92	106.16	105.92	105.68		–	–	–
	84.53	84.40	84.53	84.74	–	–	–	–
	52.86	52.86	52.96	53.00	–	–	–	–
Hydroxylamine	38.80	38.72	38.80	38.89	40.00	40.07	50.00	50.11
hydrochloride	31.04	30.98	31.04	30.98	32.00	32.07	30.00	29.94
	19.40	19.44	19.40	19.45	20.00	20.08	20.00	19.95

TABLE 2

Potentiometric determination of Hydrazine and its organic derivatives with Iodine cyanide in non-aqueous solvents

Reductant	Acetic acid medium Amount of reductant, mg			1 : 1 Acetic acid-acetic anhydride medium Amount of reductant, mg		
	Taken	Found	Error %	Taken	Found	Error %
Hydrazine hydrate	29.16	29.20	+0.15	35.20	35.14	−0,17
	21.12	21.07	−0.23	26.40	26.46	+0.22
	17.60	17.56	−0.22	17.60	17.65	+0.28
Chloralhydrazine	93.44	93.30	−0.15	87.69	87.75	+0.17
	70.08	70.17	+0.12	58.40	58.59	+0.32
	58.40	58.28	−0.21	46.72	46.84	+0.25
1 : 1 Methylphenylhydrazine	77.00	77.11	+0.14	62.80	62.92	+0.12
	57.75	57.65	−0.17	47.10	47.21	+0.23
	38.50	38.60	+0.26	31.40	31.34	−0.19
Phenylhydrazine	58.20	58.33	+0.22	61.60	61.45	−0.24
	43.65	43.74	+0.21	46.20	46.31	+0.23
	29.10	29.19	+0.31	30.80	30.72	−0.22
Benzalazine	109.60	109.39	−0.19	103.20	103.02	−0.17
	82.20	82.41	+0.25	77.40	77.52	+0.15
	54.88	54.88	+0.15	51.60	51.50	−0.20

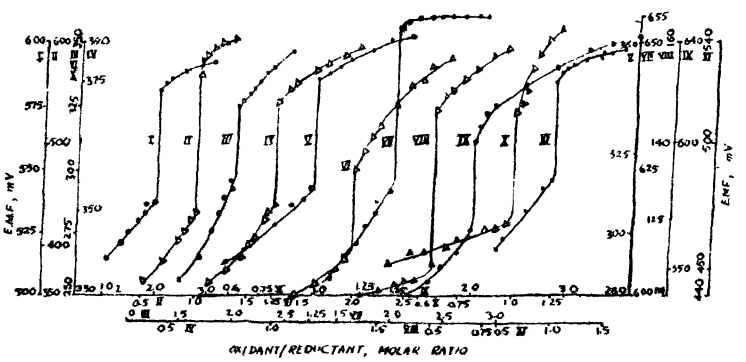


Fig. 1. Potentiometric titrations of Iodine cyanide with I, Hydrazine sulphate; II, Acetylhydrazine; III, Chloralhydrazine; IV, 1 : 1 Dimethylhydrazine hydrochloride; V, 1 : 1 Diethylhydrazine hydrochloride; VI, Phenylhydrazine hydrochloride; VII, Benzalazine; VIII, Hydroxalamine hydrochloride; IX, Benzylhydrazine hydrochloride; X, *p*-Tolylhydrazine hydrochloride; XI, 1 : 1 Methyl phenylhydrazine : In aqueous medium.

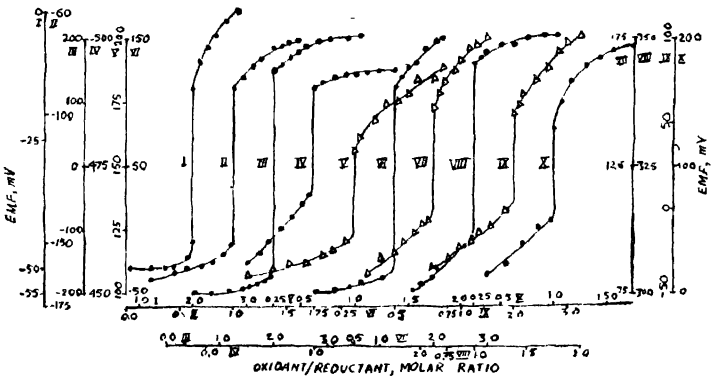


Fig. 2. Potentiometric titrations of Bromine cyanide with I, Hydrazine sulphate; II, Acetylhydrazine; III, Chloralhydrazine; IV, 1 : 1 Dimethylhydrazine hydrochloride; V, 1 : 1 Diethylhydrazine hydrochloride; VI, Hydroxylamine hydrochloride; VII. Benzylhydrazine hydrochloride; VIII, *p*-Tolylhydrazine hydrochloride; IX, Phenylhydrazine hydrochloride; X, 1 : 1 Methyl phenylhydrazine : In aqueous medium.

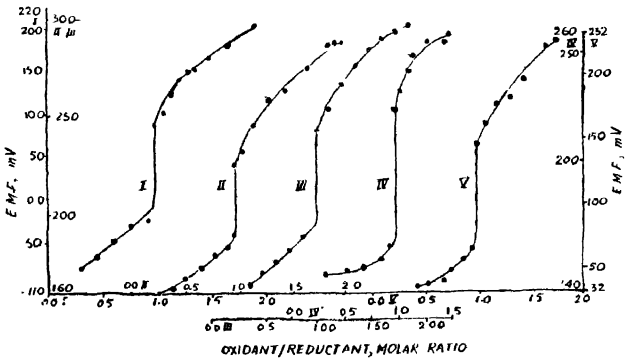


Fig. 3. Potentiometric titrations of Iodine cyanide with I, 1 : 1 Methyl phenylhydrazine; II, Phenylhydrazine; III, Chloralhydrazine; IV, Benzalazine; V, Hydrazine hydrate : In acetic acid medium.

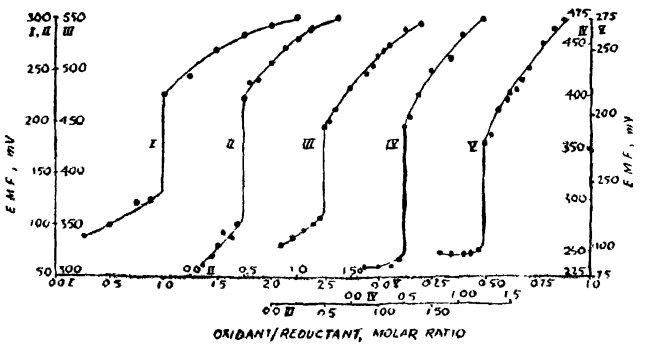


Fig. 4. Potentiometric titrations of Iodine cyanide with I, Hydrazine hydrate; II, Chloralhydrazine; III, Phenylhydrazine; IV, 1 : 1 Methyl phenylhydrazine; V, Benzalazine : In 1 : 1 acetic acid-acetic anhydride mixture.

RESULTS AND DISCUSSION

Iodine cyanide and bromine cyanide react quantitatively with hydrazine sulphate, chloralhydrazine, phenylhydrazine hydrochloride and benzylhydrazine hydrochloride in the molar ratio 2 : 1 and with acetylhydrazine, 1 : 1 dimethylhydrazine hydrochloride, 1 : 1 diethylhydrazine hydrochloride, 1 : 1 methylphenylhydrazine and *p*-tolylhydrazine hydrochloride in 1 : 1 molar ratio (Figs. 1–2). However, two equivalents of hydroxylamine hydrochloride react with one equivalent of the oxidant. Benzalazine does not consume bromine cyanide whereas it reacts with iodine cyanide at *p*H 2·7–3·2 in the molar ratio 1 : 2. 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. The role of Br^+ in the titrations is evident from the fact that hydrazine and its derivatives can be titrated with bromine cyanide quantitatively below *p*H 5·3 whereas the titrations with iodine have been successfully carried out only inb asic medium[2].

Hydrazine and its derivatives are oxidised by weak oxidizing agents in aqueous medium to nitrogen or substituted tetrazene[2,15,21]. The reactions with iodine cyanide and bromine cyanide (XCN) may, therefore, be explained as below :

$$N_2H_4+2X^+ \rightarrow N_2+4H^++2X^-$$

$$R_1NHNH_2+2X^+ \rightarrow R_1X+N_2+3H^++X^-$$

where $R_1 = C_6H_5^-$ or $C_6H_5CH_2^-$

$$CCl_3CH(OH)NHNH_2+2X^+ \rightarrow CCl_3CHO+N_2+4H^++2X^-$$

$$2CH_3CONHNH_2+2X^+ \rightarrow CH_3CONHNHCOCH_3+N_2+4H^++2X^-$$

$$2\begin{matrix}R_2\\R_3\end{matrix}\!\!>\!N\,NH_2+2X^+ \rightarrow \begin{matrix}R_2\\R_3\end{matrix}\!\!>\!NN=NN<\!\!\begin{matrix}R_2\\R_3\end{matrix} +4H^++2X^-$$

where R_2 = hydrogen or alkyl group and R_3 = alkyl or aryl group.

$$2NH_2OH+X^+ \rightarrow N_2+2H_2O+2H^++X^-$$

$$C_6H_5CHNNCH\,C_6H_5+2I^++2H_2O \rightarrow 2C_6H_5CHO+N_2+4H^++2I^-$$

The *p*H was maintained in the specific range by adding sodium bicarbonate solution, whenever necessary. Sodium bicarbonate, if present alone or in excess, decomposes hydrazine[5]. The use of iodine cyanide and bromine cyanide for these estimations has, therefore, a marked advantage over the other oxidants because these react below *p*H 5·3 avoiding all chances of air-oxidation and decomposition due to the presence of bicarbonate. The titrations are very simple to perform, quantitative and reversible.

The reactions are too slow to be followed volumetrically when acetate buffer (*p*H 4·5) is used in place of bicarbonate in these titrations. However, the results obtained are satisfactory if excess of iodine cyanide added to the hydrazine solution containing acetate buffer is titrated with thiosulphate after allowing the contents to stand for about 30 min.

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 estimated with iodine in concentrated sulphuric acid medium[22] but the titration could not be repeated and erratic results are obtained due to the reason stated above.

The end point is well marked in the absence of indicators by the abrupt appearance of a yellow colour 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[5]. The bromine cyanide titrations are slower than the corresponding iodine cyanide titrations when starch is used as an indicator. The potentiometric titrations carried out under similar conditions are slow but accurate and the jump in potential at the equivalence point is fair in each case (Figs. 1-2).

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 but also as it is formed in many redox reactions of hydrazine. Ammonia has been reported to interfere in the estimation of hydrazine with iodine in alkaline medium[26]. However, the presence of ammonium salts is found to have no effect on these titrations. Chloramine which is one of the intermediate products in the preparation of dialkylhydrazines, interferes with the titrations and the amount of the oxidant consumed is lesser than 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 iodine cyanide consumed is lesser than that required stoichiometrically. It is not unexpected as iron (III) compounds have been employed as oxidants for the estimation of hydrazine[24]. The addition of pyrophosphate makes the presence of iron (III) ineffective and the titration proceeds smoothly.

Estimation in non-aqueous media : Phenylhydrazine, chloralhydrazine, 1 : 1 methylphenylhydrazine and benzalazine react with iodine cyanide in 1 : 1 molar ratio in glacial acetic acid (Fig. 3) and in 2 : 1 molar ratio in 1 : 1 acetic acid-acetic anhydride mixture (Fig. 4). However, hydrazine hydrate consumes one equivalent of the oxidant in both the media. The reactions are quantitative only when the solutions are molar with respect to sodium acetate. Some other substituted hydrazine salts could not be estimated because of their insolubility in these solvents. The solutions acquire a yellow colour near the equivalence point and then gradually become yellowish brown. In non-aqueous 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 as below :

$$2N_2H_1+2I^+ \rightarrow NH_3+N_3H+4H^++2I^-$$

$$2C_6H_5NH\,NH_2+2I^+ \rightarrow C_6H_5NHN=NNHC_6H_5+4H^++2I^-$$

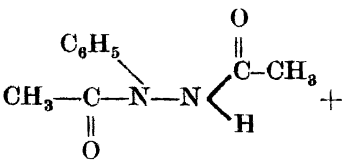
$$2\begin{matrix}CH_3\\C_6H_5\end{matrix}\!\!>NNH_2+2I^+ \rightarrow \begin{matrix}CH_3\\C_6H_5\end{matrix}\!\!>NN=NN<\!\!\begin{matrix}CH_3\\C_6H_5\end{matrix}+4H^++2I^-$$

$$2CCl_3CH(OH)NHNH_2+2I^+ \rightarrow CCl_3CH(OH)NHNHCH(OH)Cl_3C+N_2+4H^++2I^-$$

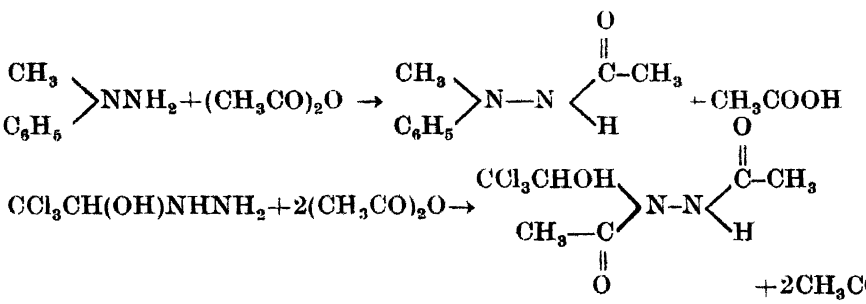
The reactions in 1 : 1 acetic acid-acetic anhydride mixture are exothermic. The mode of reaction is expected to be different due to the presence of acetic anhydride which reacts with these hydrazines as given below :[15 25]

$$H_2NNH_2+(CH_3CO)_2O \rightarrow CH_3CONHNH_2+CH_3COOH$$

$$C_6H_5NHNH_2+2(CH_3CO)_2O \rightarrow$$

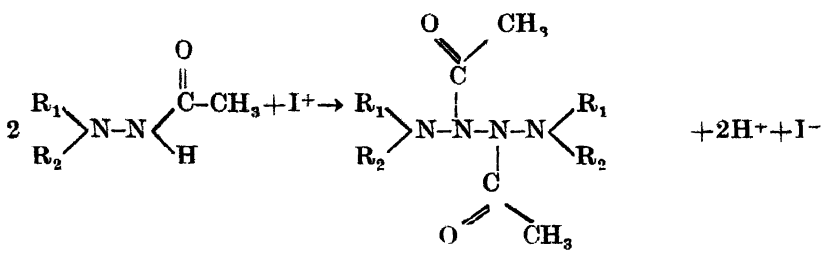


$$+2CH_3COOH$$



By analogy with the reactions explained earlier. the oxidation of these acetyl derivatives with iodine cyanide may be represented as below

$$2CH_3CONHNH_2+2I^+ \rightarrow CH_3CONHNHCOCH_3+N_2+4H^++2I^-$$



where $R_1 = CH_3CO$-, CH_3- $R_2 = C_6H_5$- or $CCl_3CH(OH)$:

It seems difficult to explain the mode of reaction of benzalazine with iodine cyanide in non-aqueous solvents.

The jump in potential in glacial acetic acid is larger than that in 1 : 1 glacial acetic acid-acetic anhydride mixture which in turn is appreciably larger than that in aqueous medium. Very accurate results have been obtained particularly in glacial acetic acid. The addition of sodium acetate which is a strong base in these solvents, is necessary as it adjusts the *p*H of the solution due to its buffering action. That glacial acetic acid is a better medium than 1 : 1 acetic acid-acetic anhydride mixture for these titrations may be due to the better adjustment of *p*H with sodium acetate in the former. Since the medium is distinctly acidic, there are no chances of air oxidation of hydrazines.

The reaction of iodine cyanide with hydrazine in ethyl alcohol does not go to completion. In fact, alcohol, acetone, formamide etc. being basic solvents do not work successfully as reaction medium for these determinations.

It is evident from these studies that the progress of the reaction is largely influenced by the nature of the solvent and the oxidising agent and that the redox reactions of iodine cyanide and bromine cyanide are the reactions of monopositive halogen.

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