CH_2Cl_2	$CH_2Cl_2 + Fe^{3\oplus}$	$CHCl_3$	$CHCl_3 + Fe^{3\oplus}$	CCl_4	$CCl_4 + Fe^{3\oplus}$	$Fe^{3\oplus}$ allein	Blindprobe
1080	410	1150	380	1210	460	580	1300

Tab. 2. Peroxidatische Indigocarmin-Entfärbung bei 37° an CH_2Cl_2, $CHCl_3$ und CCl_4 (je 12,5 mg) bei Zusatz von 0,01 mg $Fe^{3\oplus}$. Angegeben ist die Entfärbungszeit in Minuten.

1 : 6 Millionen) beschleunigen die katalytische Umsetzung, wobei $CHCl_3$ etwas ergiebiger von dieser Aktivierung Gebrauch macht (Tab. 2).

Zur Ausführung der Versuche löst man 12,5 mg der betreffenden Cl-Verbindung in 25 cm³ dest. Wasser (*) und versetzt diese Lösung nach Ablauf von 10 Min. mit 25 cm³ H_2O_2 (1,2-proz.) sowie anschließend mit 10 cm³ Indigocarminlösung (= 3,3 mg Farbstoff) bei 37°. Das einmal gründlich umgeschwenkte Reaktionsgemisch verbleibt zwecks Ermittlung der Entfärbungszeit ohne weitere Konvektion im Wasserthermostaten bei 37°. Bei Verwendung von $Fe^{3\oplus}$-Promotorionen (1 cm³ $Fe(NO_3)_3$-Lösung) erfolgt ihr Zusatz an der mit (*) bezeichneten Stelle.

Electrometric studies on the formation of alkali arsenites

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The formation and composition of different alkali arsenites, obtained by the interaction of As_2O_3 and NaOH in the ratios 1:2, 1:4 and 1:6, have been studied from p_H and Conductivity measurements. The titrations were carried out between the alkali arsenites so formed and hydrochloric acid. The p_H titrations were carried out by using glass electrode in conjunction with a saturated calomel electrode. Conductivity was measured by a conductivity meter with magic eye as visual indicator. The formation of *meta* ($NaAsO_2$), *pyro* ($Na_4As_2O_5$) and *ortho* (Na_3AsO_3) alkali arsenites were established at different p_H levels.

Meagre amount of literature is available on the electrometric studies of alkali arsenites at different p_H values. Venzetti [1] obtained alkali-*ortho*-arsenites by treating As_2O_3 with NaOH in the ratio 1 : 6. Le. Duc [2] prepared alkali-*meta*-arsenite by treating As_2O and NaOH in the desired ratio. Cernatesco and Meyer [3] observed the formation of $NaAsO_2$ when As_2O_3 and NaOH reacted in the ratio 1:2. They concluded their inferences by the freezing point depression measurements. Except for the above investigations, no systematic electrometric study appears to have been carried out on the formation and composition of alkali arsenites, particularly taking p_H into consideration. The present investigation is carried out by the coordination of p_H and conductometric titration between different alkali arsenites and hydrochloric acid.

Experimental

E. Merck's guaranted extra pure reagents Al_2O_3, NaOH and HCl were used. As_2O_3 was standardised by titrating against iodine solution and NaOH was mixed in the molar ratios of 1:2, 1:4 and 1:6 to get sodium *meta*, *pyro*, and *ortho* arsenites respectively. These were then titrated with standard hydrochloric acid. The conductometric and p_H titrations were performed by taking HCl solution in the micro-burette and arsenites solution in the conductivity and electrode cells respectively. Titration cells in both the cases were kept in an electrically maintained thermostat. Conductance was measured on a conductivity meter with magic eye as visual indicator.

p_H measurements were carried out with a cambridge p_H meter (null diflection type), standardised against standard buffer solution. Curves were plotted between the p_H (observed) and the volume of the titrant added in ml. In case of Conductometric titrations, observed conductance was corrected for the dilution effect and the curves were plotted between corrected conductance and the volume of titrant added in ml. For the sake of brevity, only one indicative diagram has been given.

Discussion

Different arsenite solutions were prepared by treating As_2O_3 and NaOH in the ratios 1:2, 1:4 and 1:6. When As_2O_3 and NaOH are mixed in the ratio 1:2, sodium *meta*-arsenite is formed. On mixing As_2O_3 to NaOH in the ratio 1:4, *pyro*-arsenite is formed and on mixing As_2O_3 and NaOH in the ratio 1 : 6, *ortho*-arsenite is formed according to the following reactions:

$$As_2O_3 + 2\,NaOH \rightarrow 2\,NaAsO2 + H_2O\,, \qquad \text{(i)}$$

$$As_2O_3 + 4\,NaOH \rightarrow Na_4As_2O_5 + 2\,H_2O\,, \qquad \text{(ii)}$$

$$As_2O_3 + 6\,NaOH \rightarrow 2\,Na_3AsO_3 + 3\,H_2O\,. \qquad \text{(iii)}$$

It is clear from figure (1) Curve A that when HCl is added to $NaAsO_2$ solution [equation (i)] a sharp deflection occurs at a point when the ratio of $NaAsO_2$ + HCl is 1 : 1 showing the formation of sodium *meta*-arsenite. The initial p_H of *meta*-arsenite solution is of the order of ten. On addition of HCl, it gradually falls and when it attains the value of eight, an abrupt fall in p_H is observed. Thus the formation of sodium *meta*-arsenite is indicated. Its formation is further confirmed from conductivity measurements (Curve A'). Conductivity first gradually rises and when the molar ratio of $NaAsO_2$ and HCl reaches 1:1, an abrupt rise

[1] B. L. Venzethi, Gazz. Chem. Ital. **55**, 106 [1925].
[2] Marc. Le. Duc, V. S. **2**, 319, 777, May 25.
[3] I. R. Cernatesco and A. Meyer, Z. physik. Chem., Abt. A. **160**, 305 [1932].

in conductivity is observed due to the higher mobility of excess $H^{\oplus}$ ions.

When the solution of arsenite is prepared according to equation (ii) and p_H titrations were carried out, two points of inflection are observed, first at the ratio of 1:2 between $Na_4As_2O_5$ and HCl and the second when their ratio is 1:4 showing the course of reaction as below:

$$As_2O_5^{4\ominus} + 2\,H^{\oplus} \rightleftharpoons 2\,AsO_2^{\ominus} + H_2O\,,$$
$$2\,AsO_2^{\ominus} + 2\,H^{\oplus} \rightleftharpoons 2\,HAsO_2\,.$$

In conductometric titrations (Curve A′), it may be noted that the conductivity first falls when the ratio of $As_2O_5^{4\ominus}$ and $H^{\oplus}$ ions is 1:2. It then increases gradually and after the ratio of $As_2O_5^{4\ominus}$ and $H^{\oplus}$ ions reaches 1:4, the conductivity abruptly rises due to the presence of excess of $H^{\oplus}$ ions. This clearly indicates the formation of *pyro*-arsenite [equation (ii)].

However, when As_2O_3 and NaOH are mixed in the ratio of 1:6, the formation of *ortho*-arsenite is indicated [equation (III)]. On titrating this *ortho*-arsenite solution with HCl it is observed both from p_H and conductometric titrations (Curves C and C′), that the points of inflection occur when 2 moles of HCl were added for 1 mole of Na_3AsO_3. On further addition of HCl, another point of inflection occurs when 3 moles of HCl were added for 1 mole of Na_3AsO_3. The reaction can be explained as follows:

$$AsO_3^{3\ominus} + 2\,H^{\oplus} \rightleftharpoons AsO_2^{\ominus} + H_2O\,,$$
$$AsO_2^{\ominus} + H^{\oplus} \rightleftharpoons HAsO_2\,.$$

It may thus be concluded that three definite sodium arsenites (*Meta*, *pyro* and *ortho*) are formed, when NaOH and As_2O_3 are mixed in the desired ratios.

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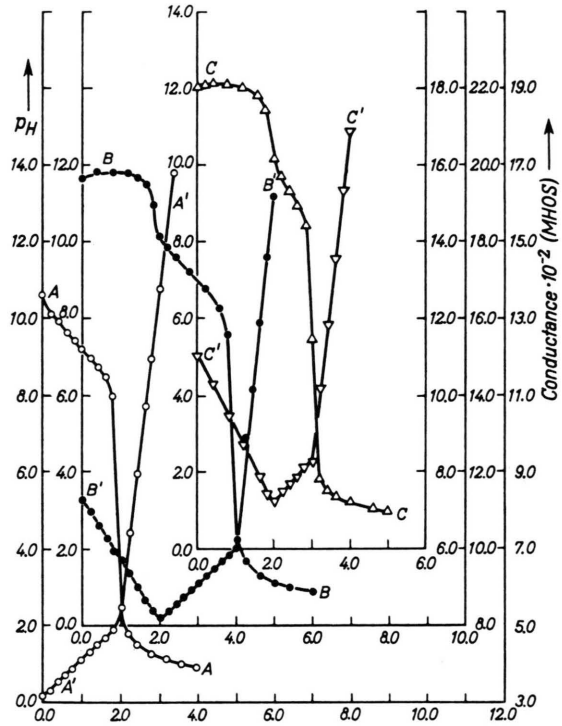

Fig. 1. Titrations of alkali arsenites with HCl. Curves A, B and C — p_H titrations andCurves A′, B′ and C′ —Conductometric titrations. A and A′ — 2 M HCl added to M/5 *meta*-arsenite, B and B′ — 2 M HCl added to M/10 *pyro*-arsenite and C and C′ — 2 M HCl added to M/10 *ortho*-arsenite (20 ml. of sodium arsenite solutions were used in each titration).

Molarity of solutions		Points of equivalence			Formula supported
HCl	Arsenites	Calculated	Observed from p_H measurements	Observed from conductivity measurements	
		Meta Arsenite (As_2O_3 : NaOH : : 1 : 2) [ml]			
2 M	M/5	2.0	1.9	1.9	
M	M/8	2.5	2.45	2.45	$NaAsO_2$
M/5	M/20	5.0	4.95	4.95	
		Pyro Arsenite (As_2O_3 : NaOH : : 1 : 4) [ml]			
2 M	M/10	2.0	2.0	1.95	
M	M/16	4.0	3.95	3.95	
		5.0	4.9	4.95	$Na_4As_2O_5$
M/20	M/250	1.6	1.55	1.6	
		3.2	3.15	3.2	
		Ortho Arsenite (As_2O_3 : NaOH : : 1 : 6) [ml]			
2 M	M/10	2.0	2.0	2.0	
		3.0	3.0	3.0	
M	M/16	2.5	2.55	2.55	Na_3AsO_3
		3.75	3.7	3.7	
M/10	M/200	2.0	2.0	1.95	
		3.0	2.95	2.95	

Table I. Summary of results of p_H and Conductometric titrations. HCl is added to 20 ml. of arsenite solutions.