

*The Polarographic Reduction of Tervalent Arsenic in  
Non-complex-forming Media.*

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The polarographic reduction of trivalent arsenic has been studied in 0.1N-solutions of hydrochloric, nitric, perchloric, and sulphuric acids. The waves obtained were not satisfactory for analytical application. When 0.001% of methylene-blue was added to the solutions in 0.1N-hydrochloric and sulphuric acids analytically satisfactory waves were obtained possessing reproducible diffusion current constants for arsenic concentrations down to  $10^{-4}$ M (or less accurately down to  $10^{-5}$ M). Gelatin was shown to be unsatisfactory as a maximum-suppressing agent owing to the marked reduction it caused in the height of the arsenic wave. The formation of arsine during the reduction has been demonstrated, and an interpretation of the various sections of the unsuppressed wave has also been advanced.

THE reduction of trivalent arsenic in dilute solutions of non-complex-forming acids gives rise to waves of high complexity which are somewhat unsatisfactory in analytical application (Kacirkova, *Coll. Czech. Chem. Comm.*, 1929, **1**, 477; Krutykova, *Zavod. Lab.*, 1940, **9**, 950; Bambach, *Ind. Eng. Chem. Anal.*, 1942, **14**, 265; Lingane, *ibid.*, 1943, **15**, 583). In general, the reduction of trivalent arsenic in the presence of complex-forming organic acids such as tartaric (Haight, *Analyt. Chem.*, 1954, **26**, 593), or its anodic oxidation in

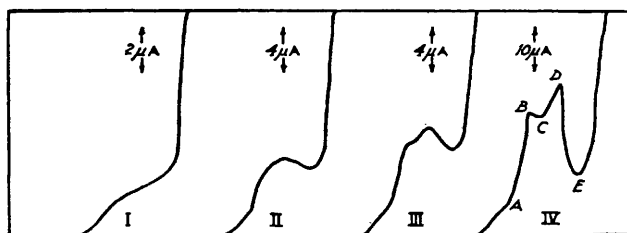


FIG. 1. 0.1N-Hydrochloric acid containing (i) 0.05, (ii) 0.15, (iii) 0.20, and (iv)  $0.60 \times 10^{-3}$ M-trivalent arsenic.

alkaline media (Kolthoff and Probst, *ibid.*, 1949, **21**, 753; Cozzi and Vivarelli, *Analyt. Chim. Acta*, 1951, **5**, 215), has appeared to be of greater practical analytical utility. The present object has been to establish analytically satisfactory conditions for the reduction of trivalent arsenic in dilute solutions of non-complex forming acids, and also to obtain information concerning the various sections of the complicated polarograms obtained with a view to their possible interpretation.

*Results and Discussion.*—*Experiments in absence of maxima-suppressors.* Typical reduction waves of trivalent arsenic in 0.1N-hydrochloric acid are shown in Fig. 1, the effect of arsenic concentration on the heights of the various sections of these waves being shown in Fig. 2. Exactly equivalent behaviour was found in 0.1N-nitric, perchloric, and sulphuric acid. These waves, obtained in absence of suppressors, were not satisfactory for analytical application. As shown in Fig. 2, the heights of the points A, B, and C did not increase linearly with the arsenic concentration, the point A, indeed, reaching a constant current value above an arsenic concentration of *ca.*  $2-3 \times 10^{-3}$ M. The point E, whose current was approximately linear with the arsenic concentration, was too close to the peak D and the final hydrogen wave to allow of accurate measurement. That the reduction

TABLE I.

$10^3[\text{As}]$ (M)	Potentials (v) vs. S.C.E.				$10^3[\text{As}]$ (M)	Potentials (v) vs. S.C.E.			
	A	B	C	D		A	B	C	D
1.02	-0.70	-0.74	-0.92	-1.07	3.06	-0.73	-0.915	-1.02	-1.19
1.28	0.70	0.87	0.94	1.12	3.56	0.73	0.92	1.02	1.20
1.52	0.71	0.88	0.95	1.16	4.08	0.75	0.93	1.02	1.21
2.04	0.72	0.91	1.02	1.19					

was irreversible was indicated by the negative movement of the potentials of the various sections of the wave on increasing the arsenic concentration (Table 1), and also by the slope of the plot of  $E - \log i/(i_d - i)$  (0.11) for waves in the arsenic concentration range  $1-2 \times 10^{-4}M$ , *i.e.*, at arsenic concentrations at which relatively simple waves are obtained (Fig. 1).

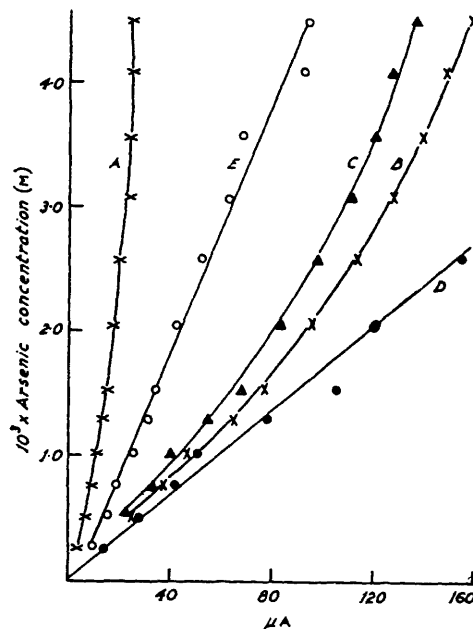
**Products of reduction.** In agreement with Kacirkova (*loc. cit.*), we could detect visually the formation of elementary arsenic, starting from the foot of the reduction wave. However, as pointed out by Lingane (*loc. cit.*), the overall height of the arsenic wave is too great to be accounted for simply by a three-electron reduction to elementary arsenic, and it is necessary to postulate an overall six-electron reduction to arsine. That some arsine is formed on electrolysis of trivalent arsenic solutions at potentials 0.1 v more negative than that of the last section of the arsenic wave has already been demonstrated by Kruykova (*loc. cit.*); her work has now been extended, by use of a modified Gutzeit technique, to find exactly those sections of the arsenic wave associated with arsine formation. It was found that at potentials up to, and including, the point *A* no arsine could be detected, whilst at all potentials from the point *B* upwards arsine was found as a product of reduction. It appears, therefore, that up to the point *A* only elementary arsenic is formed and that *A* represents the limiting current for the reduction  $As^{3+} \rightarrow As^0$ . Although it is well known that arsine, together with a large excess of hydrogen, is formed by electrolytic reduction of arsenic solutions at a mercury cathode (*e.g.*, Aumonier, *J. Soc. Chem. Ind.*, 1927, **46**, 341), this is the first occasion on which such formation of arsine has been detected at potentials below that of hydrogen evolution.

The fact that the point *A* reaches a constant height above an arsenic concentration of *ca.*  $2-3 \times 10^{-3}M$  is considered to result from the formation of a film of elementary arsenic on the surface of the mercury drop. This film interferes with the course of the electrode process, causing further reaction to occur at more negative potentials. Similar behaviour to this has been found in the polarographic reduction of quadrivalent selenium and tellurium (Lingane and Niedrach, *J. Amer. Chem. Soc.*, 1949, **71**, 196) and with bivalent germanium (Everest, *J.*, 1953, 660); in both cases analogous explanations to the above were advanced.

**Turbulence effects.** These were observed visually by addition of inert powders such as talc, charcoal, or graphite, the presence of which had no effect on the arsenic wave. From applied potentials of zero up to that of the point *B* only the normal motion of the liquid, due to the passage of the mercury drop, was observed. From *B* to the point *D* turbulence occurred, the motion of the liquid being directed upwards towards the drop, thus causing a swirling motion around the dropping electrode. At *E* the motion of the liquid was again normal. Identical behaviour was found in all four acids used. Attempts to view this turbulence in the presence of maxima-suppressors were unsuccessful since the added suppressors were simply adsorbed by the finely divided powders present.

**Effect of adding maxima-suppressors.** Three suppressors have been tried, gelatin, methylene-blue, and sodium methyl-red, the effect of increasing concentrations of these substances on the arsenic wave being illustrated in Figs. 3*a*, 3*b*, and 3*c*. Of these substances gelatin was clearly unsatisfactory owing to the marked reduction it caused in

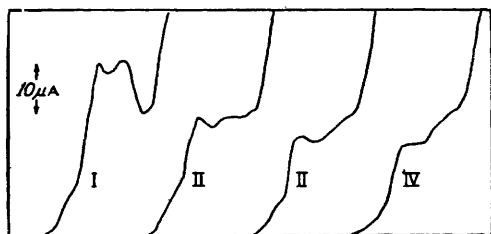
FIG. 2. Tervalent arsenic in 0.1*N*-hydrochloric acid.



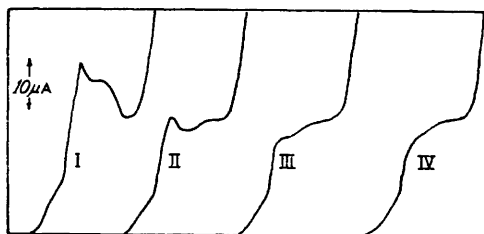
the overall wave height. In particular, with 0.003% of gelatin, the point *E* became too indistinct for its height to be measured at all. Methylene-blue was more satisfactory, addition of 0.001% eliminating the points *B*, *C*, and *D* whilst leaving the height of *E* entirely unaffected. Although addition of 0.001% of sodium methyl-red had little effect on the height of the point *E*, yet it did not completely eliminate either the point *B* or the subsequent dip in the diffusion current. The resulting waves were unsatisfactory for accurate analytical application as there was scarcely any horizontal section to the diffusion current before the onset of the hydrogen wave.

The constancy in the wave height of *E*, together with the lack of any abnormal turbulence at that point, was considered evidence that *E* represented the true diffusion current for the reduction  $\text{As}^{3+} \rightarrow \text{As}^{3-}$  ( $n = 6$ ). The fact that the point *A*, before it reaches a constant height, is approximately half the corresponding value of *E* further supports this view. The values of *I* (the diffusion current constant) for the point *E* in presence of methylene-blue are given in Table 2; these values are to be compared with the value of 8.9 for *I* found by Lingane (*loc. cit.*) in 1.0*N*-hydrochloric acid in presence of 0.01%

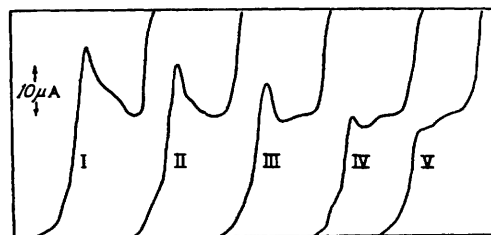
FIG. 3a-c.  $1.02 \times 10^{-3}$ M-Tervalent arsenic in 0.1*N*-hydrochloric acid containing :



3a (i) 0.001%, (ii) 0.003%, (iii) 0.006%, and (iv) 0.009% of gelatin.



3b (i) 0.00005%, (ii) 0.0002%, (iii) 0.0006%, and (iv) 0.0010% of methylene-blue.



3c (i) 0.0001%, (ii) 0.0003%, (iii) 0.0005%, (iv) 0.0010%, and (v) 0.0015% of sodium methyl-red.

of gelatin; his lower value for *I* may be due to the higher acid concentration used, but it must also be partly due to the use of gelatin as maxima-suppressor.

That the points *B*, *C*, and *D* are simply maxima is indicated both by their ready elimination by maxima-suppressors and also by the abnormal turbulence observed at all three points. As *B* is the first point on the arsenic wave at which arsine can be detected it appears that *B* can be regarded as the normal maximum of the  $\text{As}^0 \rightarrow \text{As}^{3-}$  wave (*A*-*B*). That the point *D* is not a normal maximum like *B* is shown by the fact that it appears after the  $\text{As}^0 \rightarrow \text{As}^{3-}$  wave has apparently reached a limiting value (*C*). Although no explanation can be advanced concerning the true nature of the point *D*, its behaviour appears similar to that of the delayed maximum observed by Schwaer and Suchy (*Coll. Czech. Chem. Comm.*, 1932, 4, 319) in the six-electron reduction of quadrivalent tellurium to hydrogen telluride in an ammoniacal medium. This maximum occurred after the tellurium wave had reached its limiting value, the wave returning to the limiting value after the maximum. The fact that with the arsenic wave the point *C* is higher than the point *E* is simply due to the closeness of the two peaks *B* and *D* which prevents *C* falling to the true diffusion current (*E*).

Unlike the behaviour in 0.1*N*-hydrochloric or sulphuric acid solutions of trivalent arsenic in 0.1*N*-nitric acid in presence of methylene-blue gave only poorly defined waves

which were useless for analytical application. Difficulty was also experienced in 0.1N-perchloric acid, where the addition of methylene-blue gave rise to a scarlet precipitate which caused erratic flowing from the mercury cathode.

TABLE 2.

$$t = 2.08 \text{ sec.}, m = 2.247 \text{ mg./sec.}, m^{\frac{1}{2}}t^{\frac{1}{2}} = 1.938.$$

*Arsenic trioxide in 0.1N-hydrochloric acid with 0.001% of methylene-blue.*

$10^3[\text{As}]$ (M)	Diff.		$10^3[\text{As}]$ (M)	Diff.		$10^3[\text{As}]$ (M)	Diff.	
	current, $\mu\text{A}$	$I$		current, $\mu\text{A}$	$I$		current, $\mu\text{A}$	$I$
0.253	6.25	12.7	0.910	22.25	12.6	1.310	31.75	12.5
0.506	12.50	12.7	1.012	24.50	12.5	1.520	37.0	12.6
0.708	17.25	12.6	1.112	27.50	12.8	1.720	41.0	12.4
							Mean value	12.6

*Arsenic trioxide in 0.1N-sulphuric acid with 0.001% of methylene-blue.*

0.76	19.0	12.9	1.26	31.0	12.7	1.76	43.2	12.7
1.01	25.2	12.9	1.52	37.2	12.6		Mean value	12.8

*Effect of pH.* In order to determine the exact range of pH over which reduction occurred,  $1 \times 10^{-4}\text{M}$ -arsenic solutions were examined in a series of sodium acetate-hydrochloric acid buffers, a relatively simple wave being obtained at these arsenic concentrations. As the pH was increased, the wave height decreased (from 4  $\mu\text{A}$  at pH 1.4 to 3.6  $\mu\text{A}$  at pH 2.6) whilst the half-wave potentials shifted to more negative values ( $-0.765 \text{ v}$  vs. S.C.E. at pH 1.4 to  $-0.905 \text{ v}$  at pH 2.6). Beyond pH 2.6 accurate measurement became impossible owing to the interference with the hydrogen wave, whilst above pH 4.2 the arsenic wave became completely merged with that of hydrogen. In agreement with Lingane (*loc. cit.*) no reduction of trivalent arsenic was observed in alkaline solution.

*Arsenic species present in solution.* Since the trivalent arsenic wave is unchanged in shape, height, and position in 0.1N-solutions of hydrochloric, sulphuric, nitric, and perchloric acids (in absence of suppressors), it seems certain that the same reduction process occurs in all cases, and that the arsenic is largely present in the same form in all these acid solutions. This common form of the arsenic is probably  $\text{As}_2\text{O}_3$  or a hydrated form such as  $\text{H}_3\text{AsO}_3$ . It has been observed by Krzykova (*loc. cit.*), and in an isolated case by Alimarin and Ivanov-Emin (*J. Appl. Chem. U.S.S.R.*, 1944, 12, 204), that there is a marked change in the shape of the arsenic wave on increasing the chloride concentration to *ca.* 3–4M. This change is best explained by assuming that in chloride-rich media the arsenic is present largely as chloro-complex anions such as  $\text{AsCl}_4^-$ .

#### EXPERIMENTAL

A Tinsley polarograph incorporating a D.C. amplifier and a pen recorder was used throughout. Determinations were carried out in an H-type cell incorporating an external saturated potassium chloride calomel electrode (Lingane and Laitinen, *Ind. Eng. Chem. Anal.*, 1939, 11, 504) which was immersed in a thermostat at  $25^\circ \pm 0.15^\circ$ . The resistance of this cell was less than 1000 ohms. Dissolved air was removed by passage of nitrogen. Solutions were made by dissolving 1 g. of arsenic trioxide in 500 ml. of water and dilution as required, no solutions more than ten days old being used in order to avoid ageing effects. The drop-times of the capillaries were determined at  $-1.25 \text{ v}$  against S.C.E. in 0.1N-hydrochloric acid, and the mass of mercury flowing per second was measured in air on open circuit.

*Detection of arsine.* The apparatus used consisted of a glass 30-ml. cell incorporating a mercury-pool anode and a dropping-mercury cathode. A  $4.08 \times 10^{-3}\text{M}$ -trivalent arsenic solution in 0.1N-hydrochloric acid (15 ml.) was first degassed with a stream of nitrogen and then electrolysed at the required potential for 2–3 hr. Electrolysis was then stopped and a stream of nitrogen passed through the solution to sweep out any arsine that had been formed. This nitrogen stream was then passed over mercuric chloride paper in a Gutzeit apparatus to detect the presence of arsine. Blank experiments showed that no stains were produced on the mercuric chloride paper by the simple passage of nitrogen through such solutions.

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