# REACTIONS OF ARSENIC ACID WITH PYROCATECHOL AND PYROGALLOL

J.Votava[a] and M.Bartušek

*Analytical Chemistry Department,*
*J. E. Purkyně University, 611 37 Brno*

*Dedicated to Professor S. Stankoviansky on the occasion of his 70th birthday.*

Reactions of $H_3AsO_4$ and $H_2AsO_4^-$ with pyrocatechol and pyrogallol have been studied in aqueous solutions of pH < 7 by the method of potenciometric neutralization titration. Formation of the complexes $AsL_3^-$ and $AsL_2(OH)_2^-$ has been proved, and the respective stability constants have been determined. Applicability of these complexes for alkalimetric determination of arsenic acid is discussed.

Reaction of pyrocatechol ($H_2L$) with arsenic acid in concentrated aqueous solutions was reported[1] to give the compound $H_3[AsOL_3]$ . 4 $H_2O$ which was resolved into optical antipodes and formulated[2] as $H[AsL_3]$.5 $H_2O$. Craddock and Jones[3,4] studied polarimetrically hydrolysis of the optical antipodes and found $pK_a = 2.75$ for the complex acid for which they postulated the structure $[AsL_2(HL)(H_2O)]$. The hydrolysis of the optical antipodes brought about by addition of HCl to neutral solution of the salt $K[AsL_3H_2O]$ was investigated[5], dissociation of the respective complex acid is represented by Eq. (*A*), and the $pK_a$ value given was determined from pH value of the half-neutralized 0·003M complex acid.

$$[AsL_2(HL)(H_2O)] + H_2O \rightleftharpoons [AsL_3(H_2O)]^- + H_3O^+ \; ; \; pK_a = 2.1 \text{ to } 2.2 \quad (A)$$
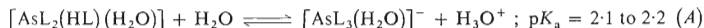
The authors[5] presume that hydrolysis produces the complex $[AsL_2OH]$ which is stable in solution. The values $2 < pK_a < 3$ given in literature for the complex of As(V) do not represent any marked acidity change as compared with free arsenic acid ($pK_a = 2.2$), whereas all the other acids (boric, germanic, molybdic ...) reacting with pyrocatechol showed acidity increase[6].

Stejskal[7] found that titration curve of 0·0025M arsenic acid at pH < 7 in the absence of pyrocatechol is the same as that found in the 0·05M-$H_2L$ medium. Complex equilibria of the reactions of $H_3AsO_4$ or $H_2AsO_4^-$ with 1,2-dihydroxybenzenes have not yet been studied.
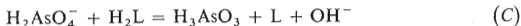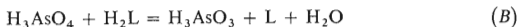
## EXPERIMENTAL

Potenciometric titrations with standard 0·1M-NaOH solution were carried out with an automatic apparatus ABU 12, TTT 11, pHM 26 and SBR (Radiometer, Copenhagen) using a glass G 202 B

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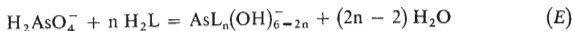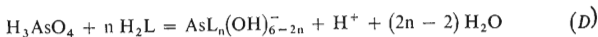[a]   Present address: Tesla, 756 61 Rožnov.

and a saturated calomel electrode. The Nernst response of the used glass electrode was proved by evaluating the titration of a strong acid with a strong base ($HNO_3$ + NaOH), and the pH meter was calibrated with phosphate buffer pH 6·50 (Radiometer) before each titration. Ionic strength of the solutions was adjusted at $I$ 0·1 by addition of potassium nitrate. Temperature during titrations was 20 ± 1°C. Activity of the proton and concentrations of the other components were used for calculations of the constants given in this report. Pyrocatechol and pyrogallol of technical grade were purified by distillation under nitrogen, symmetrical diphenylguanidine was crystallized from ethanol. The other reagents used were commercial chemicals (Lachema) of *p.a.* purity grade.


## RESULTS AND DISCUSSION

Acidity of aqueous arsenic acid is increased in the presence of excess 1,2-dihydroxy-benzene. pH Values 1·69, 1·27 and 1·34 were found in solutions of $0.1M$-$H_3AsO_4$ with $c_L$ 0, 0·4M pyrogallol and 0·4M pyrocatechol, respectively. Fig. 1 gives the neutralization course of arsenic acid with and without the presence of pyrocatechol. Complexes of As(V) with pyrocatechol were described in literature[1−5], but redox processes cannot be excluded during the reactions of these components in acid medium, too. In the case of the redox reaction arsenic acid would be reduced to arsenous acid, which does not react with excess pyrocatechol in acid medium[8], and pyrocatechol would be oxidized to *o*-benzoquinone, which itself is coloured and would undoubtedly form brown to black compounds (analogous to quinhydrone) with excess pyrocatechol. The redox reaction of pyrocatechol with arsenic acid (Eq. (*B*)) does not involve protons, and that with $H_2AsO_4^-$ anion (Eq. (*C*)) consumes one proton.

$$H_3AsO_4 + H_2L = H_3AsO_3 + L + H_2O \qquad (B)$$

$$H_2AsO_4^- + H_2L = H_3AsO_3 + L + OH^- \qquad (C)$$

The symbol L represents quinone only in Eqs (*B*) and (*C*). Experiments show that arsenic acid solution does not turn coloured on addition of pyrocatechol, and it does liberate protons, whereas the reaction of $H_2AsO_4^-$ anion with pyrocatechol does not involve protons. These experimental facts do not fit the presumption of the redox reactions (*B*) and (*C*) and can be explained by formation of complexes according to Eqs (*D*) and (*E*).

$$H_3AsO_4 + n\,H_2L = AsL_n(OH)_{6-2n}^- + H^+ + (2n-2)\,H_2O \qquad (D)$$

$$H_2AsO_4^- + n\,H_2L = AsL_n(OH)_{6-2n}^- + (2n-2)\,H_2O \qquad (E)$$

Chelates of similar type are known with B(III) (ref.[9]), Mo(VI) (ref.[10]) and Ge(IV) (ref.[11]); these complexes bind the protons less firmly than the original acids, therefore the complex formation is accompanied by acidity increase of aqueous solutions of

these acids. If in the reaction $(D)$ $n = 3$, then the weak tribasic arsenic acid (ref.[11,14] gives 2·2 – 2·4, 6·8 – 7·0 and 11·5 for $pK_{a1}$, $pK_{a2}$ and $pK_{a3}$, respectively) is transformed into strong monobasic complex acid $H[AsL_3]$. The chelate anion $AsL_3^-$ (Formula *I*) has all the 6 co-ordination positions of the central atom occupied by oxygen atoms of pyrocatechol ligands. From formula *I* it follows that the complex $AsL_3^-$ is neither base nor acid in aqueous medium, as it does not contain suitable free electron pair able to bind the proton in aqueous solution, neither does it contain acidic hydrogen
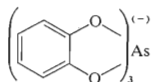


*I*

atoms. If in the reactions $(D)$ or $(E)$ is $n < 3$, it can be anticipated from analogy with B(III) and As(III) that the complex anion $AsL_n(OH)_{6-2n}^-$ will have little affinity to bind the protons. Reaction of the anion $AsL_n(OH)_{6-2n}^-$ with the proton can theoretically produce the molecule $AsL_n(OH)_{5-2n}$, but existence of analogous particles from B(III) (ref.[9]), Ge(IV) (ref.[11]) and As(III) (ref.[8]) in aqueous solutions was not proved; such reactions with the proton lead to decomposition of the complex into the starting components[15]. Experimentally it was found that addition of diphenyl-guanidinium salt to aqueous solution of the complex acid produces a white precipitate: formation of a water-insoluble salt of bulky organic cation with bulky anion $AsL_3^-$ stands in accord with the known properties of ionic associates[12].

Course of the reaction of arsenic acid with pyrocatechol can be studied by the method of potenciometric alkalimetric titration either from increased acidity of the solutions during neutralization of arsenic acid to the first degree, *i.e.* from the decreased concentration of the non-dissociated molecules $H_3AsO_4$, or from lowered consumption of base for neutralization of arsenic acid to the second degree, *i.e.* from the lowered concentration of the non-complex anion $H_2AsO_4^-$. As arsenic acid is considerably dissociated to the first degree in diluted aqueous solutions, it is more advantageous to measure the consumption of base for neutralization to the second degree which decreases with increasing concentration of the complexes in solution. Neutralization of $H_2AsO_4^-$ ($pK_a$ 6·8) is partially overlapped by neutralization of the excess pyrocatechol ($pK_a$ 9·4). For determination of $[H_2AsO_4^-]$ the Gran function[13] was used: $v \cdot 10^{const-pH} = f(v)$ involving the added volume $(v)$ of base consumed for neutralization of $H_2AsO_4^-$ and arbitrary constant (const). The Gran function was evaluated only in the region where it was experimentally proved that neutralization of dihydroxy-benzene makes not yet itself felt. Decomposition of the complexes was not observed during the titration of $H_2AsO_4^-$ lasting not longer than 10 min. If the complex were

decomposed during this titration, the amount of $H_2AsO_4^-$ anions would increase, and graph of the Gran function would not be linear. However, linear course of the Gran functions was found experimentally in a broad interval 6.0 to 7.6, the $v_e$ value was determined ($v_e$ equals $v$ at the point of equivalence) which is decreasing with increasing $c_L$, and the dependence $\log (v/(v_e - v)) \equiv \log ([H_2AsO_4^-]/[HAsO_4^{2-}]) = = f(pH)$ was calculated. This dependence is linear with the slope 0.98 to 1.10 (linear regression gave the correlation coefficient values 0.9985 to 0.9999) and gives the $pK_{a2}$ values $6.76 \pm 0.03$ at all the used pyrocatechol and pyrogallol concentrations and at $c_L = 0$. This $c_L$-independence of the $pK_{a2}$ values thus found confirms that no perceptible decomposition of the complexes takes place during titration.

After mixing arsenic acid with pyrocatechol a slow increase of acidity of the solution is observed. A series of solutions of equal total concentrations of As(V) and pyrocatechol ($c_{As}$ and $c_L$) were titrated within times of 10 minutes to 24 hours from their preparation. The titration curves of solutions older than 60 minutes are identical. The solutions titrated within 10 to 60 minutes after preparation show an increase of the reaction product with time. In the present work all the solutions were measured 1.5 to 6 hours after their preparation, $i.e.$ after reaching the equilibrium.

A series of 0.023M-$H_3AsO_4$ solutions were prepared containing the same concentration of pyrocatechol ($c_L = 0.34$M) and various concentrations of nitric acid. After the equilibrium was established these solutions were quickly neutralized to pH 4−5 and the content of free $H_2AsO_4^-$ was determined titrimetrically. In the solutions having $c_{HNO_3}$ 0, 0.02, 0.04 and 0.06M the pH before neutralization was 1.80, 1.50, 1.35 and 1.20, respectively, and the titration gave 71, 64, 56 and 52% of reacted As, respectively. The fact that at higher acidity less complex is formed confirms correctness of the presumption of the reaction $(D)$. Slightly acidic medium in which the reaction $(E)$ takes place is most favourable for formation of the complexes.

Composition and equilibrium constants of the complexes formed by reaction $(E)$ were determined in solutions of 0.037M-$KH_2AsO_4$, pH 4.5 and $c_L = 0.16$ to 0.80M; the unreacted $H_2AsO_4^-$ was determined titrimetrically. The relations $(1)-(5)$ hold for these solutions.

$$c_{As} = [H_2AsO_4^-] + [AsL(OH)_4^-] + [AsL_2(OH)_2^-] + [AsL_3^-] \qquad (1)$$

$$c_L \approx [H_2L] \gg [AsL(OH)_4^-] + 2[AsL_2(OH)_2^-] + 3[AsL_3^-] \qquad (2)$$

$$\beta_n = [AsL_n(OH)_{6-2n}^-]/[H_2AsO_4^-][H_2L]^n \qquad (3)$$

$$Y = (c_{As} - [H_2AsO_4^-])/[H_2AsO_4^-][H_2L] = \beta_1 + \beta_2[H_2L] + \beta_3[H_2L]^2 \qquad (4)$$

$$(Y - \beta_1)/[H_2L] = \beta_2 + \beta_3[H_2L] \qquad (5)$$

The dependence $Y = f(c_L)$ is non-linear and crosses the origin, hence $\beta_1 = 0$. The

function $(Y - \beta_1)/c_L = f(c_L)$ is linear, the values of the constants $\beta_1$ and $\beta_2$ given in Table I were read from the intercept under the straight line and from slope of the linear dependence $Y/[H_2L] = f([H_2L])$. Small values of the stability constants explain why the reaction of $H_3AsO_4$ or $H_2AsO_4^-$ is practically insignificant at $c_L < 0.1$M.

Fig. 1 shows that in the solution containing 0·02M $H_3AsO_4$ and 0·2M pyrocatechol there is a considerable amount of non-complexed As. If diphenylguanidinium chloride is added to this solution of complex acid up to the total concentration of 0·04M, a white voluminous precipitate is formed immediately, and the titration curve recorded 90 minutes after preparation of the solutions shows that practically all non-complexed As disappeared from the solution. In the reference solution containing the same arsenic acid and diphenylguanidinium concentrations and $c_L = 0$ no precipitate was formed, and the titration curve of non-complexed arsenic acid was not affected by the presence of the bulky organic cation.

*Reaction with pyrogallol*: Pyrogallol reacts with arsenic acid quite analogously as pyrocatechol. All the experiments described with pyrocatechol were carried out also with pyrogallol, and the results were practically identical. The complexes with pyrogallol are somewhat more stable than those with pyrocatechol (Table I).

TABLE I

Stability Constants of As(V) Chelates with Pyrocatechol and Pyrogallol Determined from Eq. (5)

| Reagent | Measured at $c_L$ (M) | cc[a] | $\beta_2$ (s)[b] | $\beta_3$ (s)[b] |
|---|---|---|---|---|
| Pyrocatechol | 0·16, 0·32, 0·40, 0·64, 0·80 | 0·9966 | 6·53 (0·02) | 8·64 (0·05) |
| Pyrogallol | 0·16, 0·32, 0·40, 0·64 | 0·9993 | 10·37 (0·04) | 28·06 (0·09) |

[a] Correlation coefficient of the linear regression $Y/[H_2L] = f([H_2L])$, [b] standard deviation.
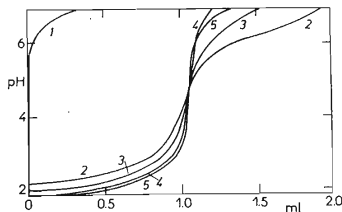


FIG. 1

Titration Curves of Neutralization of 5 ml 0·6M Pyrocatechol Solution (*1*) and 5 ml 0·02M-$H_3AsO_4$ with Standard Solution 0·1 M-NaOH at Pyrocatechol Concentrations 0 (*2*), 0·2 (*3*), 0·4 (*4*) and 0·6M (*5*)

The values $K_1 \equiv \beta_1 = 0$ of the both reagents indicate that the reaction of As(V) with $o$-dihydroxybenzenes is not a typical stepwise formation of complexes, where the $n$-th ligand is co-ordinated usually less easily than the previous $(n-1)$-th ligand $(K_n < K_{n-1})$. Analogous anomalous higher stability of $o$-dihydroxybenzene complexes having a higher number of ligands as that with As(V) was observed also with Ge(IV), where only the chelate 1 : 3 is formed in solution[11], and with Mo(VI) and W(VI), where only the chelate 1 : 2 is formed in neutral solutions, and the 1 : 1 chelate is known only in its protonated form[10].

*Alkalimetric determination of arsenic acid*: The equivalence point of titration of arsenic acid to the first degree is at pH 4·6 to 4·8. The titration curve is little steep in this region, the acidity difference of 0·02M solutions titrated to 99 and 101% being $\Delta = 0·6$ pH units. In the presence of pyrocatechol the jump at the equivalence is greater, being $\Delta = 0·9$ and 1·5 at $c_L = 0·2$ and 0·4M, respectively. Greater concentrations of pyrocatechol than 0·4M are superfluous. The comparison of titration curves for $c_L$ 0·4 and 0·6M given in Fig. 1 shows that a higher pyrocatechol concentration does not substantially increase the steepness of the curve in the equivalence region, and at pH $\approx 7$ its own consumption of base begins to make itself felt unfavourably, which caused the changed order of the curves No 5 and 4 in Fig. 1 at pH $> 6·5$. The equivalence point can be determined objectively poteciometrically from the intersect of the titration curves of two equal aliquots, one of which being titrated in 0·2 to 0·4M pyrocatechol solution and the other at $c_L = 0$ (Fig. 1). From the visual indicators for determination of arsenic acid, the mixture of 3 parts 0·1% Bromocresol Green and 1 part 0·2% Methyl Red proved suitable; the both indicators are soluble in ethanol. At the equivalence point red colour changes to violet, and immediately after the equivalence its turns to grey-green. The colour change is very sharp at $c_L = 0$, whereas in pyrocatechol solutions the colours are less clear, the colour change at the equivalence being, however, good. Pyrogallol can be used for determination of arsenic acid instead of pyrocatechol. The advantage of pyrogallol, greater stability of its complexes with As(V), is compensated by its easier oxidation by air oxygen and by higher acidity of its phenolic groups.

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