proposed that the initial product has Cr(III) bound to the carbonyl oxygen. Then the carboxylate group may ionize and form chelate or the initial product may hydrolyze to give free pyruvate or hydrate to give a monodendate complex (VII), which accounts for the small amount of pyruvate held back in the 3+ fraction. The pyruvate hydrate product (VII) is analogous to that proposed by Zanella and Taube[12] for the *p*-formylbenzoato system. The hydrolytic instability of the initial product is consistent with the generally weak coordination of ketonic oxygen, as observed for the acetone and methyl acetate complexes of pentaamminecobalt(III)[14] and the methyl isonicotinate complex $(NH_3)_5RuNC_5H_4C(OCH_3){=}OCr(OH_2)_5^{5+}$ studied by Gaunder and Taube.[15] The varying amount of chelate with acidity is attributed to the necessity to ionize the carboxylate proton in a fast equilibrium process before chelation can occur. This ionization will be suppressed at higher acidity. The sequence of ionization–hydration–chelation may be as shown in Scheme III, but the stage at which hydration occurs cannot be defined by our observations.

Experimental Section

Materials. (Pyruvato)pentaamminecobalt(III) perchlorate was prepared by published methods[1,3] and characterized by its electronic and proton NMR spectra. Chromium(II) perchlorate solutions were prepared by reduction of solutions of chromium(III) perchlorate at the appropriate acidity with amalgamated zinc.

Product Analysis. Ion-exchange separations of products were done in a cold room at 4 °C on Dowex 50W-X2 resin unless otherwise noted. Chromium was determined spectrophotometrically as chromate after oxidation with alkaline hydrogen peroxide. Free pyruvic acid was determined by the spectrophotometric method of Sokol[16] using a calibration curve based on sodium pyruvate (Sigma).

The variation of the products with acidity was determined with [Cr(II)] = 7×10^{-3} M and [Co(III)] = 5.5×10^{-3} M at ambient temperature. After reaction, the solution was exposed to dioxygen and subjected to ion exchange as described above.

Instrumentation and Kinetic Analysis. Spectrophotometric measurements generally were done on a Cary 219 spectrophotometer. Some measurements, as noted in the text, and the kinetic study of the reduction were done on a Hewlett-Packard 8451 diode-array system. Both spectrophotometers have thermostated cell blocks. The absorbance–time data for kinetic runs were analyzed by nonlinear least-squares and errors quoted are one standard deviation. All kinetic measurements are at 25 °C in 1.0 M $NaClO_4/HClO_4$. In the reduction studies, the $[H^+]$ was varied between 0.020 and 0.040 M and the $[Cr^{2+}]$ between 1.4×10^{-3} and 5.45×10^{-3} M.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support for this work.

Registry No. II, 43227-19-6; V, 121072-63-7; Cr^{2+}, 22541-79-3.

Supplementary Material Available: Table S1, listing the reagent concentrations and observed and calculated rate constants for the reduction of (pyruvato)pentaamminecobalt(III) by chromium(II) (1 page). Ordering information is given on any current masthead page.

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Arsenic(IV). A Pulse-Radiolysis Study

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Four As(IV) species assumed to be $As(OH)_4$ and $HAsO_3^-$ and the corresponding bases $As(OH)_3O^-$ and AsO_3^{2-} (pK_a = 7.38 and 7.81, respectively) were observed by the pulse-radiolysis technique in aqueous arsenious acid, arsenite, and arsenate solutions. $As(OH)_4$ and $As(OH)_3O^-$ were observed in acid and weakly alkaline solution by the reaction of arsenious acid or arsenite with OH. $HAsO_3^-$ and/or AsO_3^{2-} are formed by the reaction of e^-_{aq} with $H_2AsO_4^-$ and $HAsO_4^{2-}$; AsO_3^{2-} is formed by the reaction of arsenite with O^- in strongly alkaline solution and by the reaction of arsenite with the carbonate radical anion CO_3^-. $As(OH)_4$ and $As(OH)_3O^-$ convert into $HAsO_3^-$ and AsO_3^{2-} by general-base-catalyzed reactions. In acid solution an equilibrium between $As(OH)_4$ and $HAsO_3^-$ is observed. The kinetics of dehydration of $As(OH)_4$ suggest a slow dehydration step catalyzed by H^+ followed by protolysis:

$$As(OH)_4 \underset{k_r}{\overset{k_f}{\rightleftharpoons}} H_2AsO_3 + H_2O \rightleftarrows HAsO_3^- + H_2O + H^+$$

$k_f/k_r \sim 10^{-3}$–10^{-2}; $k_f = 2.4 \times 10^4 + 3.8 \times 10^8[H^+]\ s^{-1}$. The equilibrium constant for the overall reaction is 1.4×10^{-4}; the standard enthalpy of reaction is 10.4 kJ mol^{-1}. The energy and the entropy of activation for the uncatalyzed and the H^+-catalyzed dehydration of $As(OH)_4$ are 23 kJ mol^{-1} and −93 J $mol^{-1}\ K^{-1}$ and 25 kJ mol^{-1} and −6 J $mol^{-1}\ K^{-1}$, respectively. By comparison with activation parameters of other dehydration–hydration processes, these values are taken to suggest a cyclic transition state containing an extra water molecule. While $As(OH)_4$ and $As(OH)_3O^-$ react with O_2 to yield directly HO_2 and O_2^-, $HAsO_3^-$ and AsO_3^{2-} react with O_2 with formation of a relatively stable complex that subsequently decomposes to HO_2 or O_2^- in reactions catalyzed by H^+ and OH^-. The various As(IV) species disappear in second-order reactions with rate constants ranging from 2×10^7 to $2 \times 10^9\ dm^3\ mol^{-1}\ s^{-1}$. As(IV) species are both very strong oxidants and reductants. (Estimates for the standard reduction potentials $As(OH)_4 + e^- + H^+ \rightarrow As(OH)_3 + H_2O$ and $H_3AsO_4 + e^- + H^+ \rightarrow As(OH)_4$ are 2.4 and −1.2 V, respectively.)

Introduction

The present knowledge of the properties of As(IV) in aqueous solution stems from earlier steady-state and pulse-radiolysis experiments on As(III) and As(V) solutions[1-3] and from stoichiometric and kinetic studies of the oxidation of arsenious acid by peroxodisulfate in presence of a ferrous salt as an inductor.[4] The steady-state radiolysis and the study of the induced oxidation of arsenious acid by peroxodisulfate have shown that As(IV) is a powerful reducing agent that is capable of reducing molecular

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[†] Aarhus University.
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(1) Daniels, M. *J. Phys. Chem.* **1962**, *66*, 1473, 1475.
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oxygen to the superoxide radical anion, O_2^-. Pulse-radiolysis studies[2] have shown that an As(IV) species with an absorption band centered at 335 nm is formed by a rapid reaction of hydroxyl radicals with arsenite at pH = 10.7 ($k = 8.4 \times 10^9$ dm^3 mol^{-1} s^{-1}).[5] The hydrated electron reacts relatively slow with arsenate ($k = 1.9 \times 10^8$ dm^3 mol^{-1} s^{-1} at pH = 11.0).[3] No transient absorption resulting from the latter reaction has been reported.

Different As(IV) species may result from the different types of reactions.[6,7] We have in the present work studied As(IV) produced by reducing arsenate with the hydrated electron, by oxidizing arsenite with the carbonate radical anion, and by the reaction of OH and O^- with arsenious acid and arsenite.

Experimental Section

All aqueous solutions were prepared with water that, after distillation, had been passed through a Millipore ultrapurification system. Arsenite and arsenious acid solutions were prepared by dissolving As_2O_3 in a NaOH solution and adjusting to the desired pH by adding a buffer, $HClO_4$ or NaOH. NaOH (99.999% purity) and $HClO_4$ (Vycor Distilled) were from G. Frederick Smith Co. As_2O_3 was from Johnson Matthey Chemical Ltd. with certificate of analysis (Batch No. S 70313). $Na_2HAsO_4 \cdot 7H_2O$ (Baker Analyzed reagent) and HCOONa (Fisher Scientific) were recrystallized three times, once from a solution containing 10^{-4} mol dm^{-3} diethylenetriaminepentaacetate (Sigma Chemical Co.) and twice from water. All other chemicals were Reagent Grade. Gasses were ultrahigh purity from Matheson Co. or were from Dansk Ilt og Brint of similar purity. Deaeration and saturation of solutions with gasses were performed by bubbling. Solutions containing both O_2 and N_2O were prepared either by mixing in syringes two solutions, one saturated with O_2 and the other with N_2O, or by bubbling the solutions with gaseous mixtures of O_2 and N_2O at 1 atm. The composition of the gas mixture was controlled by flowmeters that measured the flow of the two gases before they were mixed. The readings of the flowmeters were calibrated in terms of the O_2 concentration in solutions containing both O_2 and N_2O. The O_2 concentration was determined by the Winkler method.[8] The concentration of N_2O was calculated from the measured O_2 concentration and the known solubility of O_2 and N_2O in water at 1 atm.[9]

Changes in As(III) concentration by radiolysis was measured iodometrically. I_3^- was measured spectrophotometrically. The molar absorption coefficient at 350 nm was taken as equal to 2.58×10^4 dm^3 mol^{-1} s^{-1}.[10] The UV spectra of arsenious acid at pH ~7, arsenic acid in 1 mol dm^{-3} perchloric acid, arsenious acid–arsenite at pH = 9 and 9.5, monohydrogen arsenate at pH = 9.4, and dihydrogen arsenate at pH = 4 were measured between 190 and 250 nm. The spectra were recorded on a Cary 210 or a Cary 219 spectrophotometer. The spectrophotometers were flushed with N_2 for measurements below 210 nm.

Pulse radiolysis was carried out at BNL with a 2-MeV Van de Graaff accelerator and at Risø with a 10-MeV linac. The experimental setups at the two laboratories are as described previously.[11,12] Steady-state radiolysis was carried out with a ^{60}Co γ-source. Dosimetry was carried out with the $(SCN)_2^-$ dosimeter with $G = 6.13$ and $\epsilon_{472} = 7575$ dm^3 mol^{-1} cm^{-1} [13] or with the hexacyanoferrate(II) dosimeter with $G = 5.9$ and $\epsilon_{420} = 1000$ dm^3 mol^{-1} cm^{-1}.

Stopped-flow experiments with HO_2/O_2^- were carried out with a modified Durrum Model D-110 stopped-flow spectrophotometer equipped with an HO_2/O_2^- generating plasma lamp.[14]

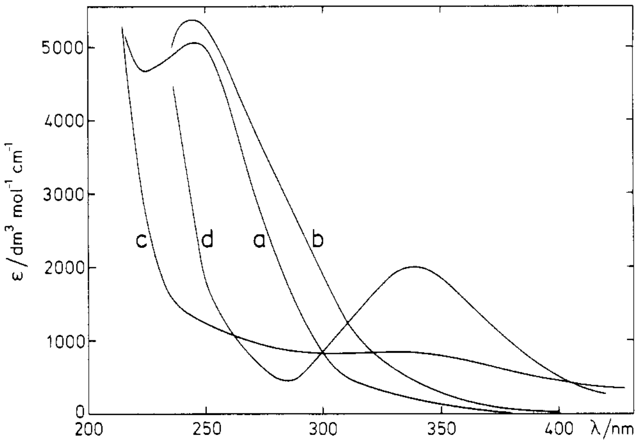

Figure 1. Spectra 25 °C of (a) $As(OH)_4$, (b) $As(OH)_3O^-$, (c) $HAsO_3^-$, and (d) AsO_3^{2-} obtained from absorbances of irradiated (dose ~ 0.5 krad) N_2O-saturated 10^{-3} mol dm^{-3} As(III) solutions at pH 5.6 (a and c) and at pH 9.4 (b and d). Spectra a and b were calculated from absorbances extrapolated to zero time after irradiation, and the spectra c and d, by extrapolation to infinite time. The extrapolations were made by assuming exponential decay of $As(OH)_4$ and $As(OH)_3O^-$ into $HAsO_3^-$ and AsO_3^{2-} (see text).

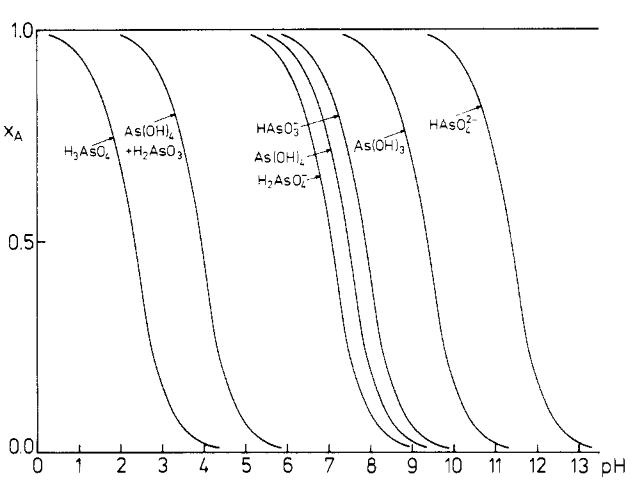

Figure 2. Bjerrum plot of the As(V) acids H_3AsO_4, $H_2AsO_4^-$, and $HAsO_4^{2-}$; of the As(IV) acids $As(OH)_4 + H_2AsO_3$ in equilibrium, $As(OH)_4$, and $HAsO_3^-$; and of the As(III) acid $As(OH)_3$. Key: abscissa, pH; ordinate, $x_A \equiv [A]/([A] + [B])$, where [A] and [B] are the concentrations of the corresponding acid and base, respectively.

pH measurements were taken with an ORION Research instrument Model 611 or a Radiometer pH M 64 Research pH meter using a Corning combination electrode or a Radiometer G 202C glass electrode and a Radiometer K701 calomel electrode. The combination electrode reacted sluggishly in ClO_4^--containing solutions probably due to a precipitation of $KClO_4$ in the porous plug of the salt bridge. Considerable improvement of performance of the electrode was obtained by interchanging the saturated KCl solution in the electrode with a 3 mol dm^{-3} NaCl solution. pH calibrations were made with Radiometer or Fisher standard buffers. pH was generally determined to within ±0.02 pH unit.

In experiments with the Van de Graff accelerator the temperature was varied between 10.0 ± 0.5 and 60.0 ± 0.5 °C. In experiments with the linac the temperature was ambient, 23 ± 2 °C.

Unless otherwise stated the experiments were carried out at 25.0 °C at an ionic strength adjusted to 0.1 mol dm^{-3} with $NaClO_4$. Computations were carried out with use of Research Software RSI, BBN Software Corp., Boston, MA.

Results and Discussion

The various reactions and equilibria for the different As(IV) species are given in Table I; the UV spectra are shown in Figure 1. Protolytic equilibria of acids of As(V), As(IV), and As(III) are depicted in Figure 2.

As(IV) Produced by Oxidation of As(III) by OH or O^-. To avoid interference from e^-_{aq} with reactants or products, the arsenite and arsenious acid solutions were saturated with N_2O at 1 atm

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Table I. Summary of Reactions

reaction	rate const,[a] pK values, equilibrium consts, and standard enthalpy of reacn/$\Delta H°$[f]
$As(OH)_3 + OH \rightarrow As(OH)_4$	$k_3 = 8.5 \times 10^9$ dm^3 mol^{-1} s^{-1}
$As(OH)_2O^- + O^- \rightarrow AsO_3^{2-} + H_2O$	$k_4 = 2 \times 10^9$ dm^3 mol^{-1} s^{-1}
$H_2AsO_3 = HAsO_3^- + H^+$	$K_{10} = 10^{-3}–10^{-2}$
$As(OH)_4 \rightleftarrows H_2AsO_3 + H_2O$	$k_9^{H_2O} = 2.4 \times 10^4$ s^{-1} [b]
	$k_9^{H^+} = 4.0 \times 10^8$ dm^3 mol^{-1} s^{-1} [b]
	$k_9^{H_2O} = 2.3 \times 10^4$ s^{-1} [c]
	$k_9^{H^+} = 3.6 \times 10^8$ dm^3 mol^{-1} s^{-1} [c]
$As(OH)_4 = HAsO_3^- + H^+ + H_2O$	p$K_6 = 3.64 \pm 0.05$
	p$K_{a6} = 3.85 \pm 0.05$[d]
	$\Delta H_6° = (10.4 \pm 0.9)$ kJ mol^{-1}
$As(OH)_4 = As(OH)_3O^- + H^+$	p$K_7 = 7.26 \pm 0.06$
	p$K_{a7} = 7.38 \pm 0.06$[d]
$HAsO_3^- = AsO_3^{2-} + H^+$	p$K_{12} = 7.57 \pm 0.04$
	p$K_{a12} = 7.81 \pm 0.04$[d]
$As(OH)_3O^- \rightleftarrows HAsO_3^- + H_2O$	$K_{11} = 4 \times 10^3$ (base-catalyzed reacns)
$As(OH)_2O^- + CO_3^{\bullet -} + 2OH^- \rightarrow AsO_3^{2-} + CO_3^{2-} + 2H_2O$	$k_{20} = 1.1 \times 10^8$ dm^3 mol^{-1} s^{-1}
$H_2AsO_4^- + e^-_{aq} + (H^+) \rightarrow HAsO_3^- + H_2O$	$k_{22} \sim 2 \times 10^9$ dm^3 mol^{-1} s^{-1} [e]
$HAsO_4^{2-} + e^-_{aq} \rightarrow AsO_3^{2-} + OH^-$	$k_{23} \sim 2 \times 10^8$ dm^3 mol^{-1} s^{-1} [e]
$2As(OH)_4 \rightarrow As(III) + As(V)$	$k_{27} = 8.4 \times 10^8$ dm^3 mol^{-1} s^{-1}
$As(OH)_4 + HAsO_3^- \rightarrow As(III) + AsV)$	$k_{28} = 2.0 \times 10^9$ dm^3 mol^{-1} s^{-1}
$2HAsO_3^- \rightarrow As(III) + As(V)$	$k_{29} = 4.5 \times 10^8$ dm^3 mol^{-1} s^{-1}
$2AsO_3^{2-} \rightarrow As(III) + As(V)$	$k_{30} = 1.9 \times 10^7$ dm^3 mol^{-1} s^{-1}
$HAsO_3^- + AsO_3^{2-} \rightarrow As(III) + As(V)$	$k_{31} = 4.8 \times 10^8$ dm^3 mol^{-1} s^{-1}
$As(OH)_4 + O_2 \rightarrow As(V) + HO_2/O_2^-$	$k_{33a} = 1.4 \times 10^9$ dm^3 mol^{-1} s^{-1}
$As(OH)_3O^- + O_2 \rightarrow As(V) + O_2^-$	$k_{33b} = 1.1 \times 10^9$ dm^3 mol^{-1} s^{-1}
$HAsO_3^- + O_2 \rightarrow As(IV)–O_2^-$	$k_{34a} \sim 10^9$ dm^3 mol^{-1} s^{-1}
$AsO_3^{2-} + O_2 \rightarrow As(IV)–O_2$	$k_{34b} = 1.4 \times 10^9$ dm^3 mol^{-1} s^{-1}
$As(IV)\text{-}O_2 \xrightarrow{H^+} As(V) + HO_2/O_2^-$	$k_{35a} \sim 10^{10}$ dm^3 mol^{-1} s^{-1}
$As(IV)\text{-}O_2 \xrightarrow{OH^-} As(V) + O_2^-$	$k_{35b} = 3.1 \times 10^4$ dm^3 mol^{-1} s^{-1}

[a] Estimated error 10–20%. [b] $K_{10} = 10^{-3}$. [c] $K_{10} = 10^{-2}$. [d] pK values extrapolated to zero ionic strength by means of Güntelberg's formula for activity coefficients.[19] [e] Ionic strength ~ 0. Ionic strength = 0.1 mol dm^{-3}.

($[N_2O] = 0.026$ mol dm^{-3}). N_2O reacts fast with e^-_{aq}, converting it into O^-

$$N_2O + e^-_{aq} \rightarrow N_2 + O^- \qquad k_1 = 9.1 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}\,{}^{15} \tag{1}$$

$$OH = O^- + H^+ \qquad pK_2 = 11.9^{16} \tag{2}$$

The rate constants for the reactions

$$As(OH)_3 + OH \rightarrow As(IV) \qquad k_3 = (8.5 \pm 0.9) \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \tag{3}$$

$$As(OH)_2O^- + O^- \rightarrow As(IV) \qquad k_4 = (2.0 \pm 0.2) \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \tag{4}$$

were determined from measured pseudo-first-order rate constants in the wavelength range from 220 to 340 nm. k_3 was determined from absorbance measurements after pulse irradiation of 10^{-4} mol dm^{-3} arsenious acid solutions at pH = 2 and pH = 5.6 with doses ranging from 0.15 to 0.4 krad. k_4 was determined from similar measurements with 2×10^{-4} mol dm^{-3} arsenite solutions at pH 13. Because of interference from subsequent reactions (see below) a determination of the rate constant for the reaction

$$As(OH)_2O^- + OH \rightarrow As(IV) \tag{3a}$$

was not attempted.

Four different As(IV) species denoted by a–d in Figure 1 were observed in the pH range 2–13. Observations described below suggest an assignment of $As(OH)_4$, $As(OH)_3O^-$, $HAsO_3^-$, and AsO_3^{2-}, respectively, to these species. Species a is formed by reaction 3 and species b by reactions 3 and 3a. Species a was observed at pH < 6 and species b at pH = 8.5–10. In the pH range 7–8 an acid–base equilibrium between species a and b was observed (Figure 2). At pH < 3, species a disappears by a second-order process, the rate of which depends only slightly on pH. No additional transient absorbance change was observed during the decay. The relative spectrum of species a was independent of pH. A decrease of absorbance of species a observed at pH < 4 could be explained by the reaction

$$e^-_{aq} + H^+ \rightarrow H \qquad k_5 = 2.3 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1}\text{s}^{-1}\,{}^{17} \tag{5}$$

At pH > 3 subsequent first-order processes appear by which species c and d are formed, species c in H^+- and base-catalyzed processes, and species d in base-catalyzed processes. Species d was furthermore formed by reaction 4. The final disappearance of As(IV) takes place by subsequent second-order processes. At the doses used (0.02–0.5 krad) the first- and second-order processes were well separated. No change in the spectra of species a–d was observed by varying the As(III) concentration from 2×10^{-4} to 10^{-2} mol dm^{-3} and the temperature from 10 to 60 °C. In the pH range 3–5 a first-order process leads to a mixture of species a and c in protolytic equilibrium (Figure 2). At pH = 5–7, only species c was observed; species d was observed at pH > 9. Composite spectra composed of the spectra of species c and d in acid–base equilibrium were observed at pH = 7–8 (Figure 2). Since species a and b appear to be the corresponding acid and base, it is apparent that the equilibrium between species a and c is not a simple protolytic equilibrium. This is supported by the observation that the rate constant for the first-order process by which species a transforms into species c is several orders of magnitude smaller than one might expect for a simple protolysis[18] (see reaction 9, Table I, and Figure 3) and furthermore by the observation that the first-order rate constant for the absorbance change increases in a nonlinear way with acidity, displaying a positive curvature (Figure 3).

The apparent pK value for the equilibrium between species a and c was determined from the relation

$$pH = pK_6 + \log((\epsilon_a - \epsilon)/(\epsilon - \epsilon_c)) \tag{6}$$

between corresponding values of pH and the molar absorption coefficient, ϵ, of the equilibrium mixture of species a and c. ϵ_a is the molar absorption coefficient of species a and ϵ_c the molar

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[18] Bell, R. P. *The Proton in Chemistry*, 2nd ed.; Chapman and Hall: London, 1973.

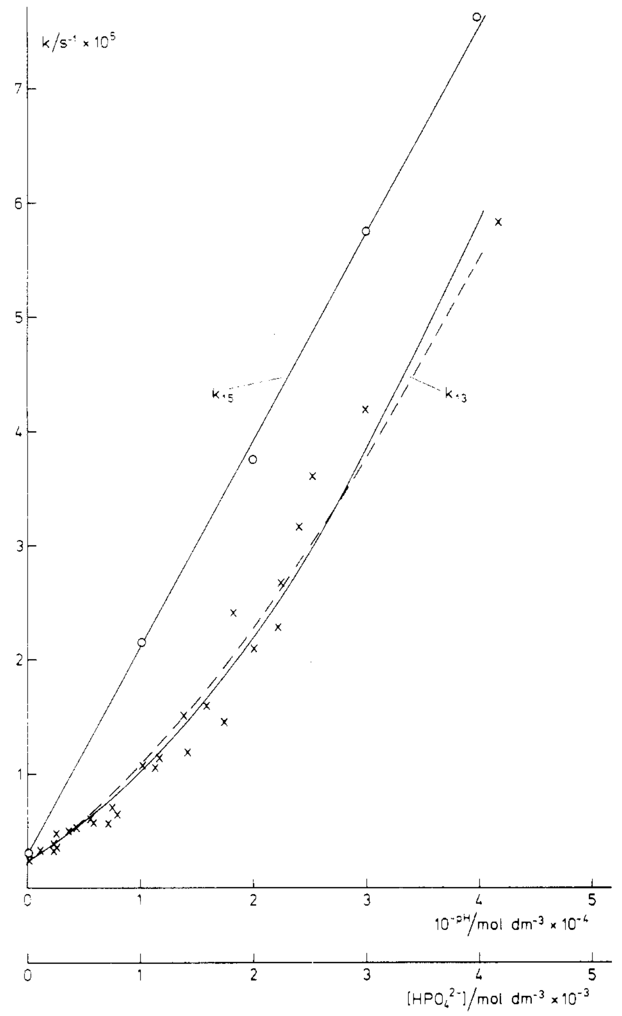

Figure 3. *x*, the rate constant k_{13} at 25 °C for the approach toward the equilibrium $As(OH)_4 = HAsO_3^- + H_2O + H^+$ plotted against pH. The solid curve is k_{13} computed from eq 14a with $pK_6 = 3.64$, $k_9^{H_2O} = 2.3 \times 10^4$ dm^3 mol^{-1} s^{-1}, $k_9^{H^+} = 3.6 \times 10^8$ dm^3 mol^{-1} s^{-1}, and $Q = 1$ (see text). The dashed curve is calculated from eq 14a with $pK_6 = 3.64$, $k^{H_2O} = 2.4 \times 10^4$ s^{-1}, $k_9^{H+} = 4.0 \times 10^8$ dm^3 mol^{-1} s^{-1}, and $k_{10}/k_{-10} = 10^{-3}$. The open circles denote the pseudo-first-order rate constants at 25.0 °C for the phosphate-catalyzed dehydration of $As(OH)_4/As(OH)_3O^-$ at pH = 6.86 (k_{15}) plotted against the concentration of HPO_4^{2-}.

absorption of species c measured at pH = 5–6 after equilibrium between species a and c had been reached. Corresponding values of ϵ at 245 nm and pH were measured at ionic strengths of 0.002 and 0.1 mol dm^{-3}. The data at ionic strength 0.1 mol dm^{-3} are shown in Figure 4. The straight line represents a least-squares fit to eq 6. The slope does not deviate significantly from the theoretical value of 1.0. We find $pK_6 = 3.78 \pm 0.05$ at ionic strength 0.002 mol dm^{-3} and $pK_6 = 3.64 \pm 0.05$ at ionic strength 0.1 mol dm^{-3}. From the values of pK_6 at the two ionic strengths we may deduce that the As(IV) species a is uncharged since only in that case does an extrapolation of the two pK_6 values to zero ionic strength lead to values that are identical within experimental error. Thus we find the values 3.82 ± 0.05 and 3.88 ± 0.05 from the two pK_6 values by using Güntelberg's formula for activity coefficients.[19] In the following we shall denote pK values extrapolated to zero ionic strength by pK_a.

Since the equilibrium between species a and b appears to be a simple protolytic equilibrium with a pK value characteristic of a very weak oxoacid with an equal number of hydrogen and oxygen atoms,[20,21] we suggest that OH, similar to several other reactions of OH,[22,23] oxidized arsenious acid and arsenite by addition. Accordingly, reactions 3 and 3a should read

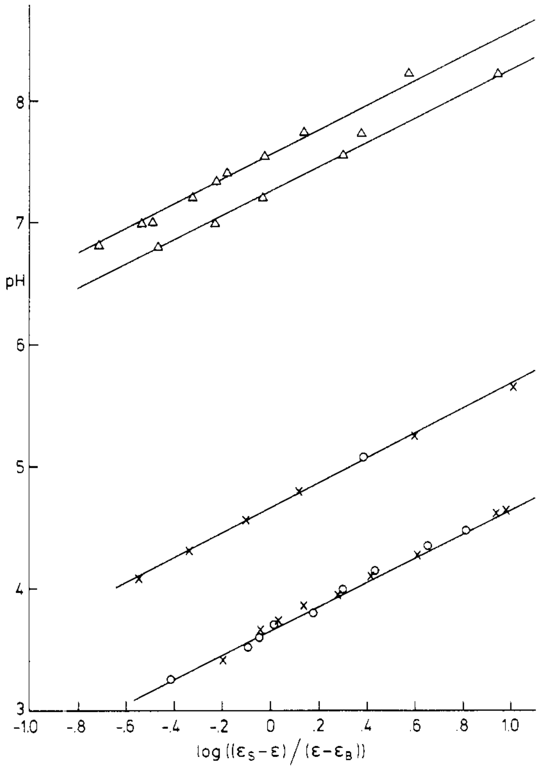

Figure 4. pH versus log $((\epsilon_S - \epsilon)/(\epsilon - \epsilon_B))$. ϵ_S and ϵ_B are the molar absorption coefficients of acid and base forms, while ϵ is the molar absorption coefficient of an equilibrium mixture of the acids and bases. Acid–base pairs from top to bottom: $HAsO_3^-/AsO_3^{2-}$; $As(OH)_4/As(OH)_3O^-$; HO_2/O_2^-; $As(OH)_4/HAsO_3^-$. For details of measurements see text. Arsenious acid concentrations are (△) 2×10^{-4}, (×) 10^{-3}, and (○) 10^{-2} mol dm^{-3} at 25 °C.

$$As(OH)_3 + OH \rightarrow As(OH)_4 \qquad (3)$$

$$As(OH)_2O^- + OH \rightarrow As(OH)_3O^- \qquad (3a)$$

The protolytic equilibrium between species a and b is thus

$$As(OH)_4 = As(OH)_3O^- + H^+ \qquad pK_7 = 7.26 \qquad (7)$$

pK_7 was determined at an ionic strength of 0.1 mol dm^{-3} in 2×10^{-3} mol dm^{-3} phosphate and borate buffers from the molar absorption coefficients, ϵ, at 290 nm as function of pH. The data were fitted to the three-parameter equation

$$\epsilon = \epsilon_{As(OH)_4} + (\epsilon_{As(OH)_4} - \epsilon_{As(OH)_3O^-})/(1 + 10^{pK_7 - pH}) \qquad (8)$$

where $\epsilon_{As(OH)_4}$ and $\epsilon_{As(OH)_3O^-}$ are the molar absorption coefficients of $As(OH)_4$ and $As(OH)_3O^-$, respectively. The data are presented in Figure 4. By extrapolation to zero ionic strength using Güntelberg's formula for activity coefficients,[19] we find $pK_{a7} = 7.38 \pm 0.06$ (see also Figure 2).

The following mechanism fits the kinetics for approaching equilibrium between $As(OH)_4$ and species c. The fact that $pK_{a6} < pK_{a7}$ suggests that an acid stronger than $As(OH)_4$ is formed from $As(OH)_4$. We suggest that $As(OH)_4$ dehydrates relatively slowly with formation of H_2AsO_3, which then dissociates in a fast step.

$$As(OH)_4 \rightleftarrows H_2AsO_3 + H_2O \rightleftarrows HAsO_3^- + H^+ + H_2O \qquad (9),(-9),(10),(-10)$$

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Table II. Catalytic Constants, *k*, for the Dehydration of $As(OH)_4$ and $As(OH)_3O^-$

base B	As(IV)	$pK_{HB} - pK_{As(IV)}$	$k/dm^3\ mol^{-1}\ s^{-1\,a}$	$k/dm^3\ mol^{-1}\ s^{-1\,b}$	$p_s{}^c$	$q_s{}^c$	$p_c{}^d$	$q_c{}^d$
H_2O	$As(OH)_4$	−9.1	4.3×10^2	4.3×10^2	4	1	3	2
$H_2PO_4^-$		−5.2	6.8×10^6	6.8×10^6			3	1
HPO_4^{2-}		−0.2	5×10^8	5×10^8			2	2
H_2O	$As(OH_3O^-$	−13.7	$<2 \times 10^2$	$<2 \times 10^2$	3	2	3	2
$H_2PO_4^-$		−9.8	...	...			3	1
HPO_4^{2-}		−4.8	3×10^7	10^7			2	2
$As(OH)_2O$		−2.7	1.4×10^8	8×10^7			3	1
$B(OH)_4^-$		−2.8	8.5×10^7	5×10^7			3	4
OH^-		3.7	8.1×10^9	5×10^9			2	1

[a] Measured at the ionic strength $\mu = 0.1$ mol dm^{-3}. [b] At $\mu = 0$ mol dm^{-3} calculated from Güntelberg's formula for activity coefficients.[18] [c] Statistical factors for acid and base forms of As(IV). [d] Statistical factors for acid and base forms of the catalyst.

The overall equilibrium (9),(−9),(10),(−10) is depicted in Figure 2.

Similarly, the conversion of $As(OH)_3O^-$ into species c is assigned to the dehydration of $As(OH)_3O^-$

$$As(OH)_3O^- \rightleftarrows HAsO_3^- + H_2O \qquad (11),(-11)$$

Reaction −11 was not observed since the equilibrium (11),(−11) is displaced to the right ($K_{11} = K_6/K_7 = 4 \times 10^3$). The conversion of $As(OH)_3O^-$ into species d is assigned to reaction 11 and a subsequent protolysis of $HAsO_3^-$

$$HAsO_3^- = AsO_3^{2-} + H^+ \qquad pK_{12} = 7.57 \pm 0.04 \qquad (12)$$

Thus reaction 4 could proceed as

$$As(OH)_2O^- + O^- \rightarrow As(OH)_2O_2^{2-} \rightarrow AsO_3^{2-} + H_2O \qquad (4a)$$

pK_{12} was determined at an ionic strength of 0.1 mol dm^{-3} from absorbance measurements at 340 nm in a manner similar to that described above for the determination of pK_7. The data are shown in Figure 4. By extrapolation to zero ionic strength, we find $pK_{a12} = 7.81 \pm 0.04$ (see also Figure 2).

The fact that no absorbance change was observed at low pH (pH < 3) that could be assigned to a formation of H_2AsO_3 suggests that $[H_2AsO_3]/[As(OH)_4] = k_9/k_{-9} \ll 1$. Since the acid dissociation constant $K_{a10} = k_{10}/k_{-10}$ is expected to be 10^{-2}–10^{-3}[20,21] and $K_{a6} = k_9k_{10}/k_{-9}k_{-10} = 10^{-3.85}$, we find $[H_2AsO_3]/[As(OH)_4]$ to be 10^{-2}–10^{-1}.

The observation that the process of approaching equilibrium between $As(OH)_4$ and $HAsO_3^-$ is of first order indicates that a steady-state approximation with $d[H_2AsO_3]/dt = 0$ is valid or alternatively that H_2AsO_3 and $HAsO_3^-$ from the start of the reaction are in protolytic equilibrium with each other.

Taking the steady-state approximation to be valid, we may express the first-order rate constant by

$$k_{13} = (k_9k_{10} + k_{-9}k_{-10}[H^+]/f_\pm^2)/(k_{-9} + k_{10}) \qquad (13)$$

where $f_\pm$ is the mean activity coefficient of dissociated H_2AsO_3 ($H^+ + HAsO_3^-$).

Assuming that H_2AsO_3 is in protolytic equilibrium with $HAsO_3^-$ during the reaction, we find

$$k_{13} = k_9 + k_{-9}k_{-10}[H^+]/f_\pm^2/(k_{10} + k_{-10}[H^+]/f_\pm^2) \qquad (14)$$

The fact that the plot of k_{13} against $[H^+]$ shows a positive curvature indicates that k_9 and k_{-9} increase with acidity. Assuming that k_9 and k_{-9} contain a term that is proportional to $[H^+]$, we may express k_9 by $k_9 = k_9{}^{H_2O} + k_9{}^{H^+}[H^+] = k_9{}^{H_2O}(1 + k_H[H^+])$ and k_{-9} by $k_{-9} = k_{-9}{}^{H_2O} + k_{-9}{}^{H^+}[H^+] = k_{-9}{}^{H_2O}(1 + k_H[H^+])$. Introducing the expression for k_9, $K_6 = K_{a6}/f_\pm$, and $[H^+] = 10^{-pH}/f_\pm$ into eq 14, we obtain

$$k_{13}/(1 + Q10^{pK_6-pH}) = k_9{}^{H_2O}(1 + k_H[H^+]) \qquad (14a)$$

where $Q = (1 + 10^{-pH}f_\pm k_{-10}/k_{10})^{-1}$.

k_{13} was measured at varying pH > 3.3 (Figure 3). Figure 5 shows plots of $k_{13}/(1 + Q10^{pK_6-pH})$ against $[H^+]$ for $k_{10}/k_{-10} = 10^{-3}$ and 10^{-2} and for $Q = 1.00$. It is apparent that the approximation $Q = 1.00$ may be used for $k_{10}/k_{-10} > 10^{-2}$. The plot with $Q = 1.00$ and with $k_{10}/k_{-10} = 10^{-3}$ both appear to be linear. Thus k_{10}/k_{-10} cannot be found from the present measurements of k_{13}.

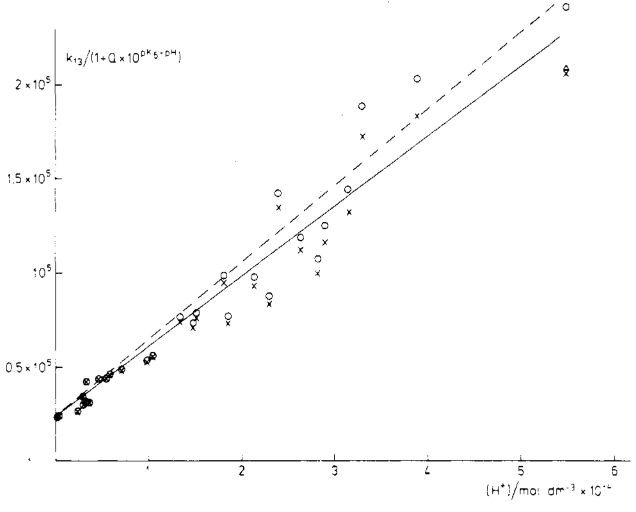

Figure 5. $k_{13}/(1 + Q10^{pK_6-pH})$ plotted against $[H^+]$: (×) calculated with $Q = 1$; (○ and △) calculated with $k_{10}/k_{-10} = 10^{-3}$ and 10^{-2}, respectively. The solid straight line represents a least-squares fit to ×; the dashed straight line represents a least-squares fit to ○. Temperature was 25 °C (see eq 14a and text).

However, $k_9{}^{H^+}$ and $k_9{}^{H_2O}$ are rather insensitive to changes in k_{10}/k_{-10} for $k_{10}/k_{-10} > 10^{-3}$. For $k_{10}/k_{-10} > 10^{-2}$ we find from the slope of the straight line using the approximation $Q = 1.00$, $k_9{}^{H^+} = k_9{}^{H_2O}k_H = (3.6 \pm 0.4) \times 10^8$ $dm^3\ mol^{-1}\ s^{-1}$. The intercept gives $k_9{}^{H_2O} = (2.3 \pm 0.1) \times 10^4\ s^{-1}$. From $k_9k_{10}/k_{-9}k_{-10} = 10^{-3.85}$, we find $k_{-9}{}^{H^+} = 2.5 \times 10^{10}$ $dm^3\ mol^{-1}\ s^{-1}$ and $k_{-9}{}^{H_2O} = 1.6 \times 10^6\ s^{-1}$.

Similarly for $k_{10}/k_{-10} = 10^{-3}$, we find $k_9{}^{H^+} = (4.0 \pm 0.4) \times 10^8$ $dm^3\ mol^{-1}\ s^{-1}$ and $k_9{}^{H_2O} = (2.4 \pm 0.1) \times 10^4\ s^{-1}$, leading to $k_{-9}{}^{H^+} = 2.8 \times 10^9$ $dm^3\ mol^{-1}\ s^{-1}$ and $k_{-9}{}^{H_2O} = 1.7 \times 10^5\ s^{-1}$.

Note that eq 14a with $Q = 1.00$ may be obtained from eq 13 by neglecting k_{-9} in comparison to k_{10}.

A least-squares treatment of the data using eq 13 where we do not neglect k_{-9} and choose $k_{-10} = 5 \times 10^{10}$ $dm^3\ mol^{-1}\ s^{-1}$, a value commonly accepted for the reaction of a proton with a negatively charged base,[18] leads to values for $k_9{}^{H_2O}$ and $k_9{}^{H^+}$ that are indistinguishable from the values determined from eq 14a.

The dehydration steps 9 and 11 were found to be catalyzed by the bases B^- = dihydrogen phosphate, monohydrogen phosphate, arsenite, borate, and hydroxide. The rate constants k_9 and k_{11} were found to increase linearly with the base concentration. The catalytic constants were determined at an ionic strength of 0.1 mol dm^{-3}. k_9 was assumed to be independent of ionic strength. Values for catalytic constants for reaction 11 at zero ionic strength were determined by use of Güntelberg's formula for activity coefficients[19] (Table II). The catalytic constants $k_9{}^{H_2PO_4^-}$, $k_{11}{}^{As(OH)_2O^-}$, and $k_{11}{}^{B(OH)_4^-}$ were determined from the slope of plots of k_9 or k_{11} at constant pH against the base concentration. $k_{11}{}^{OH^-}$ was determined from measurements of k_{11} in arsenite solutions at varying pH from the slope of a plot of $k_{11} - k_{11}{}^{As(OH)_2O^-}[As(OH)_2O^-]$ against 10^{-pH}. Extrapolation to zero for 10^{-pH} leads to an estimate of $k_{11}{}^{H_2O} < 10^4\ s^{-1}$. $k_9{}^{HPO_4^{2-}}$ was determined from measurements of the rate constant for dehydration, k_{15}, for

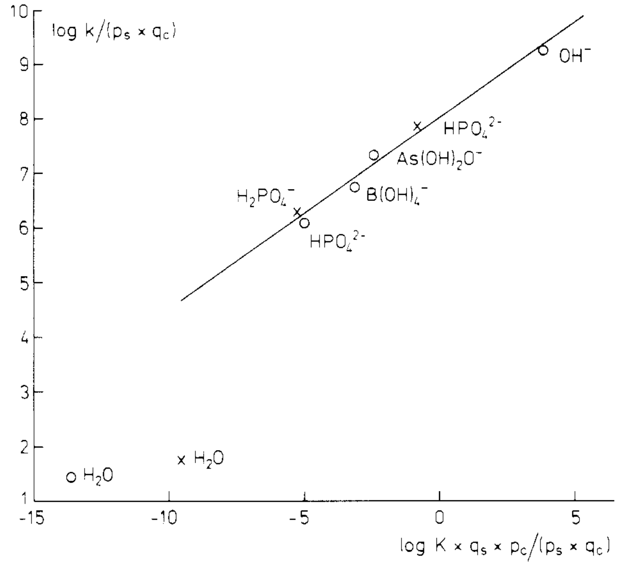

Figure 6. Brønsted plot of rate constants for the base-catalyzed dehydration of $As(OH)_4$ and $As(OH)_3O^-$ (see eq 18 and text). Temperature was 25 °C.

$[H_2PO_4^-] = [HPO_4^{2-}]$ varying between 5×10^{-4} and 2×10^{-3} mol dm^{-3}. k_{15} may be expressed by

$$k_{15} = xk_9^{H_2O} + (1 - x)k_{11}^{H_2O} + (xk_9^{H_2PO_4^-} + (1 - x)k_{11}^{H_2PO_4^-})[H_2PO_4^-] + (xk_9^{HPO_4^{2-}} + (1 - x)k_{11}^{HPO_4^{2-}})[HPO_4^{2-}] \quad (15)$$

where $x = [As(OH)_4]/([As(OH)_4] + [As(OH)_3O^-]) = 1/(1 + 10^{pH-pK_7})$. Introducing pH = 6.86, $pK_7 = 7.26$, and the values for $k_9^{H_2PO_4^-}$ and $k_{11}^{HPO_4^{2-}}$ (Table II) into eq 15 and assuming that $k_{11}^{H_2PO_4^-}$ can be neglected, we find from the slope of a plot of k_{15} against $[HPO_4^{2-}]$ (Figure 3) $k_9^{HPO_4^{2-}} = 5 \times 10^8$ dm^3 mol^{-1} s^{-1} (Table II).

Also shown in Table II are the equilibrium constants $K_{16} = K_{a7}/K_{HB}$ and $K_{17} = K_{As(OH)_3O^-}/K_{HB}$ for the equilibria

$$As(OH)_4 + B^- = As(OH)_3O^- + HB \quad (16)$$

$$As(OH)_3O^- + B^- = As(OH)_2O_2^{2-} + HB \quad (17)$$

The acidity constant $K_{As(OH)_3O^-}$ is not known. By analogy with other acid oxoanions[20,21] $K_{As(OH)_3O^-}$ is taken as equal to 10^{-12}.

Figure 6 shows a Brønsted plot.[18] As customary, the reaction with water (the uncatalyzed reaction) is taken to be of second order with a rate constant equal $k_9^{H_2O}/55.5$ and the acidity constant of water is taken equal $10^{-14}/55.5$. With the exception of the values for water, the data obey the linear relationship characteristic for a general-base catalysis[18]

$$\log (k/(p_sq_c)) = \beta \log (Kq_sp_c/(p_sq_c)) \quad (18)$$

with $\beta = 0.35$.

In eq 18, k stands for a catalytic constant and K for the corresponding equilibrium constant K_{16} or K_{17}. p_s, q_s, p_c, and q_c are the appropriate statistical factors,[18] p_s of $As(OH)_4$ or $As(OH)_3O^-$ as an acid, p_c of HB, q_s of $As(OH)_3O^-$ and $As(OH)_2O^{2-}$ as bases, and q_c of B^-.

The value for $\beta = 0.35$ is similar to values found for the base catalysis of hydration of ketones and aldehydes.[18] Also the activation parameters for the dehydration of $As(OH)_4$ are similar to those that have been observed in hydration–dehydration reaction involving a C=O group.

The activation parameters for the uncatalyzed reaction 9 ($E_{a9}^{H_2O}$, $\Delta S_9^{\ddagger H_2O}$) and for reaction 9 catalyzed by H^+ ($E_{a9}^{H^+}$, $\Delta S_9^{\ddagger H^+}$) are shown in Table III. $\Delta H_6° = 10.4 \pm 0.9$ kJ mol^{-1} (Table I) and the activation energy E_{a13} for the overall reaction were determined from the measurements of pK_6 and $\ln k_{13}$ at temperatures varying between 10 and 60 °C (Figure 7). $E_{a9}^{H_2O}$ and $E_{a9}^{H^+}$ were determined from eq 19, which may be derived from eq 14 by differentiation of $\ln k_{13}$ with respect to the absolute temperature.

Table III. Activation Parameters at 298 K for the Uncatalyzed and the H^+-Catalyzed Dehydration of $As(OH)_4$ and of $(CH_2Cl)_2C(OH)_2$[23]

	$As(OH)_4$			$(CH_2Cl)_2C(OH)_2$		
	E_a/ kJ mol^{-1}	$\Delta S^\ddagger$/ J mol^{-1} K^{-1}		E_a/ kJ mol^{-1}	$\Delta S^\ddagger$/ J mol^{-1} K^{-1}	
uncatalyzed	23	−93[a]	−126[b]	50	−127[a,c]	−160[b,c]
H^+-catalyzed	25	−6	−6	65	−100	−100

[a] Monomolecular dehydration; standard state for water = $H_2O(l)$. [b] Reaction with one molecule of water, standard state for water = 1 mol dm^{-3}. [c] Estimated from data in ref 23.

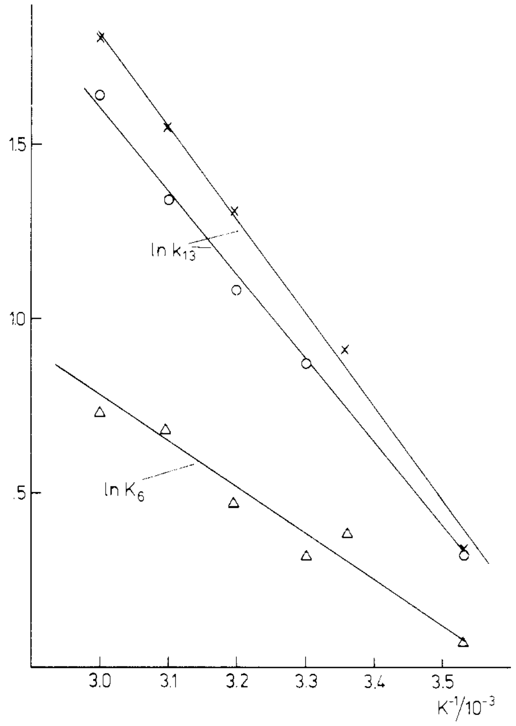

Figure 7. $\ln k_{13}$ (×) at pH 3.76 and (O) at pH 5.7 and $\ln K_6$ (Δ) (all quantities plus an arbitrary constant) plotted against the reciprocal of the absolute temperature.

$$E_{a13} = (k_9^{H_2O}E_{a9}^{H_2O} + k_9^{H^+}[H^+]E_{a9}^{H^+})/(k_9^{H_2O} + [H^+]k_9^{H^+}) - \Delta H_6° 10^{pK_6-pH}/(1 + 10^{-pK_6-pH}) \quad (19)$$

The values for $E_{a9}^{H_2O}$ and $E_{a9}^{H^+}$ in Table III were found from $E_{a13} = 23.4 \pm 0.7$ kJ mol^{-1} determined at pH = 5.7 ($[H^+] = 2.6 \times 10^{-6}$ mol dm^{-3}) and $E_{a13} = 20.2 \pm 0.7$ kJ mol^{-1} determined at pH = 3.76 ($[H^+] = 2.3 \times 10^{-4}$ mol dm^{-3}), $\Delta H_6°$, and the values for $k_9^{H_2O}$, $k_9^{H^+}$, and pK_6 determined at 25.0 °C.

Note that $E_{a9}^{H_2O} > E_{a9}^{H^+}$, $\Delta S_9^{\ddagger H_2O} < \Delta S_9^{\ddagger H^+}$ and that $\Delta S_9^{\ddagger H_2O}$ has a large negative value despite the fact that the uncatalyzed reaction formally is a monomolecular reaction. The same pattern is found for the hydration of chloral and 1,3-dichloroacetone in aqueous dioxane.[24,25] Table III shows the activation parameters for dehydration of the *gem*-diol that is formed by hydration of 1,3-dichloroacetone. Other processes that show similarities are the acid–base-catalyzed oxygen isotope exchange between iodate and water, brought about by hydration–dehydration of iodate species,[26] and the dehydration of the octahedral periodate anion $H_4IO_6^-$, which similar to the dehydration of $As(OH)_4$ proceeds with a large negative entropy of activation.[27]

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The kinetic studies suggest that the transition state of the uncatalyzed reactions are cyclic and contain extra water molecules.[24,25] The binding of extra water molecules should result in a substantial loss of entropy. On replacement of a water molecule in the transition state by the acid or basic catalyst, the loss of entropy is diminished.[24,25] This model has been verified by recent ab initio SCF–MO calculations of possible transition states for the hydration of formaldehyde,[28] carbon dioxide,[29] and ketene.[30] It was shown for all three reactions that the lowest Gibbs energy of activation was obtained with a hydrogen-bonded, planar, hexagonal transition state containing one extra, "ancillary",[28] water molecule. Hence we suggewst that the uncatalyzed dehydration of $As(OH)_4$ also proceeds by a concerted reaction via a hexagonal transition state consisting of $As(OH)_4$ and a water molecule. In Table III is shown the entropy of activation calculated with the assumption that $As(OH)_4$ dehydrates in a reaction with one water molecule (standard state for water 1 mol dm^{-3}).

Formation of As(IV) by Electron-Transfer Reactions. The carbonate radical anion, $CO_3^{\bullet-}$ rapidly oxidizes arsenite to AsO_3^{2-}

$$CO_3^{\bullet-} + As(OH)_2O^- + 2OH^- \rightarrow CO_3^{2-} + AsO_3^{2-} + 2H_2O \qquad (20)$$

$$k_{20} = (1.1 \pm 0.1) \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

k_{20} was determined under pseudo-first-order rate conditions by following the formation of AsO_3^{2-} at 335 nm as well as the disappearance of $CO_3^{\bullet-}$ at 600 nm[31] in a N_2O-saturated 5×10^{-4} mol dm^{-3} arsenite solution at pH = 10 containing 2×10^{-3} mol dm^{-3} arsenite. Under these conditions OH reacts preferentially with CO_3^{2-} [32]

$$CO_3^{2-} + OH \rightarrow OH^- + CO_3^{\bullet-} \qquad (21)$$

In contrast, arsenate is generally not easily reduced to As(IV) by electron transfer. No reaction of the strongly reducing CO_2^- [33] with $H_2AsO_4^-$ and $HAsO_4^{2-}$ and of e^-_{aq} with AsO_4^{3-} was detected, and the reaction of e^-_{aq} with $H_2AsO_4^-$ and $HAsO_4^{2-}$ was found to be relatively slow.

The transient spectra recorded after the decay of e^-_{aq} were similar to those assigned above to $HAsO_3^-$ and AsO_3^{2-}, respectively. Since $As(OH)_4$ and $As(OH)_3O^-$ were not observed, we may conclude that the dehydration of the electron adducts $H_2AsO_4^{2-}$ and $HAsO_4^{3-}$ proceeds at a faster rate than does the protonation of $H_2AsO_4^{2-}$ and $HAsO_4^{3-}$, which otherwise would have yielded the relatively stable $As(OH)_4$ and $As(OH)_3O^-$.

The rate constants for

$$H_2AsO_4^- + e^-_{aq} + (H^+) \rightarrow HAsO_3^- + H_2O \qquad k_{22} = 2 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \qquad (22)$$

$$HAsO_4^{2-} + e^-_{aq} \rightarrow AsO_3^{2-} + OH^- \qquad k_{23} = 2 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \qquad (23)$$

were determined from measurements of the pseudo-first-order rate constants for disappearance of e^-_{aq} at 700 nm in 10^{-3}–10^{-2} mol dm^{-3} arsenate solutions at pH = 5 and 9, respectively. The failure to observe any reaction of AsO_4^{3-} with e^-_{aq} under the present experimental conditions suggests a rate constant smaller than 10^6 dm^3 mol^{-1} s^{-1}.

The reaction of CO_2^- with arsenate was studied by γ-radiolysis. A N_2O-saturated 10^{-3} mol dm^{-3} arsenate solution at pH = 8 containing 10^{-2} mol dm^{-3} HCOONa was γ-irradiated with a dose of 1.2 krad. CO_2^- is produced by the reactions[34]

$$HCOO^- + H \rightarrow H_2 + CO_2^- \qquad (24)$$

$$HCOO^- + OH \rightarrow H_2O + CO_2^- \qquad (25)$$

An iodometric analysis showed that less than 10% of the theoretical yield of As(III) was formed by the irradiation implying that no reaction takes place between CO_2^- and arsenate.

Kinetics for Disappearance of As(IV). Similar to many other inorganic oxoacid or oxoanion radicals,[35] all As(IV) species disappear by second-order processes in what appear to be bimolecular diffusion-controlled reactions.

The rate constants were determined in the following way. Since under the present conditions protolytic and hydration-dehydration equilibria are maintained during the disappearance of As(IV) species, we may at pH < 6 (where the species $As(OH)_4$ and $HAsO_3^-$ predominate) express the rate constant for the disapperance of the equilibrium mixture of $As(OH)_4$ and $HAsO_3^-$ by

$$k_{26} = (k_{27} + k_{28}10^{pH-pK_6} + k_{29}10^{2pH-2pK_6})/(1 + 10^{pH-pK_6})^2 \qquad (26)$$

where k_{27}, k_{28}, and k_{29} are the rate constants for

$$2As(OH)_4 \rightarrow As(III) + As(V) \qquad k_{27} = (8.4 \pm 0.8) \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \qquad (27)$$

$$As(OH)_4 + HAsO_3^- \rightarrow As(III) + As(V) \qquad k_{28} = (2.0 \pm 0.2) \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \qquad (28)$$

$$2HAsO_3^- \rightarrow As(III) + As(V) \qquad k_{29} = (4.5 \pm 0.5) \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \qquad (29)$$

k_{27}, k_{28}, and k_{29} were determined by means of eq 26 from measurements of k_{26} at pH = 2.0, 3.0, 3.84, and 5.4.

At pH > 6 the predominant As(IV) species are $HAsO_3^-$ and AsO_3^{2-}. The rate constants

$$AsO_3^{2-} + HAsO_3^- \rightarrow As(III) + As(V) \qquad k_{30} = (4.8 \pm 0.4) \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \qquad (30)$$

$$2AsO_3^{2-} \rightarrow As(III) + As(V) \qquad k_{31} = (1.9 \pm 0.3) \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \qquad (31)$$

were determined by means of

$$k_{32} = (k_{29} + k_{30}10^{pH-pK_{12}} + k_{31}10^{2pH-2pK_{12}})/(1 + 10^{pH-pK_{12}})^2 \qquad (32)$$

from measurements of k_{32} at pH = 7.00, 7.82, 10.0, and 13.0.

Reactions of As(IV) with O_2. The As(IV) species has been suggested as an intermediate in the Cu(II)-catalyzed oxidation of alkaline arsenite solutions by molecular oxygen.[36] The reaction

$$As(IV) + O_2 \rightarrow As(V) + O_2^-/HO_2 \qquad (33)$$

and a reaction with the formation of an intermediate complex As(IV)–O_2

$$As(IV) + O_2 \rightarrow As(IV){-}O_2 \rightarrow As(V) + O_2^-/HO_2 \qquad (34),(35)$$

have been proposed in order to explain the effect of molecular oxygen on the stoichiometry and kinetics of reactions in which As(IV) is believed to be formed as an intermediate.[1,4] We have verified both types of reactions; $As(OH)_4$ and $As(OH)_3O^-$ react according to the eq 33 and $HAsO_3^-$ and AsO_2^{2-} according to the eq 34. The rate constants are close to that of a diffusion-controlled reaction (k_{33} and k_{34} = 10^9 to 1.4×10^9 dm^3 mol^{-1} s^{-1}) (Table I). The decomposition of the complex into O_2^-/HO_2 and As(V) was very slow in neutral and slightly alkaline solution. The rate

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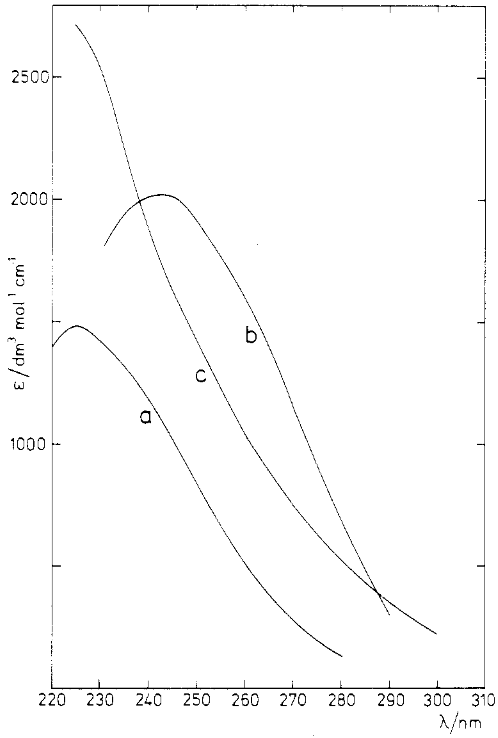

Figure 8. Spectra of O_2-containing As(III) solutions ([As(III)] = 10^{-3} mol dm^{-2}, ionic strength = 0.1 mol dm^{-3}, and T = 25.0 °C): (a) predominantly HO_2 (pH = 3, [O_2] = 1.3 × 10^{-4} mol dm^{-3}, N_2O = 2.3 × 10^{-2} mol dm^{-3}); (b) predominantly O_2^- (pH = 9.1, [O_2] = 3.8 × 10^{-4} mol dm^{-3}); (c) predominantly As(IV)–O_2 (pH = 9.1, [O_2] = 10^{-4} mol dm^{-3}; [N_2O] = 2.4 × 10^{-2} mol dm^{-3}; 10^{-2} mol dm^{-3} of Na_2HPO_4 added).

of decomposition was measured at pH ~ 5 and in strongly alkaline solution (pH > 12) only.

$$\text{As(IV)–O}_2 + \text{H}^+ \rightarrow \text{As(V)} + \text{O}_2^-/\text{HO}_2 \qquad k_{35a} \approx 10^{10}\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1} \tag{35a}$$

$$\text{As(IV)–O}_2 + \text{OH}^- \rightarrow \text{As(V)} + \text{O}_2^- \qquad k_{35b} = (3.1 \pm 0.3) \times 10^4\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1} \tag{35b}$$

These conclusions are based on the following observations.

By electron-pulse irradiation of arsenious acid/arsenite solutions containing O_2 and N_2O, two types of transients were observed. They grow in by pseudo-first-order processes at rates proportional to the oxygen concentration. One of these transients was assigned to HO_2/O_2^- and the other to the complex As(IV)–O_2. The spectra of the transients are shown in Figure 8. The assignment to HO_2/O_2^- is based on similarities of the spectra and decay kinetics at varying pH.[37] In agreement with published data for HO_2/O_2^-,[37] we measured the rate constants 3 × 10^6 dm^3 mol^{-1} s^{-1} and 2 × 10^6 dm^3 mol^{-1} s^{-1} at pH = 3.1 and 6.4, respectively, for the second-order disappearance. In strongly alkaline solution, the decay was very slow. The rate of decay was greatly enhanced by addition of Cu(II). These observations are also in agreement with the present assignment.[37,38] The change of the spectrum with pH displayed a pK value of 4.68 at an ionic strength of 0.1 mol dm^{-3}, which corresponds to pK_a = 4.80, a generally accepted value.[37] The pK value was determined by use of an equation similar to eq 6 from measurements of corresponding values of ϵ at 260 nm and pH. ϵ_S and ϵ_B were taken equal to 570 dm^3 mol^{-1} cm^{-1} and 1750 dm^3 mol^{-1} s^{-1}, respectively (Figure 4).

Reaction 33 is indicated by the observation that HO_2 and O_2^- are formed whenever the concentrations of oxygen and $As(OH)_4$ or $As(OH)_3O^-$ are high, i.e. when the rate of dehydration of $As(OH)_4$ and $As(OH)_3O^-$ is slow or when the equilibrium concentration of $As(OH)_4$ is high compared to that of $HAsO_3^-$ (pH < 3). Conversely, we observed As(IV)–O_2 at small O_2 concentrations and when the rate of dehydration of $As(OH)_4$ or $As(OH)_3O^-$ was fast. Thus, O_2^- was observed in 9 × 10^{-4} mol dm^{-3} arsenious acid/arsenite solution at pH = 9.1 containing 3.8 × 10^{-4} mol dm^{-3} oxygen, whereas by lowering the O_2 concentration to 9 × 10^{-5} mol dm^{-3} and adding 10^{-2} mol dm^{-3} HPO_4^{2-}, the spectrum assigned to As(IV)–O_2 appeared. Likewise, HO_2/O_2^- was observed at pH = 5–6 in unbuffered solutions containing 3 × 10^{-4} mol dm^{-3} O_2 and As(IV)–O_2 in a solution containing 6 × 10^{-5} mol dm^{-3} O_2 and 10^{-2} mol dm^{-3} phosphate buffer.

The rate of decay observed for As(IV)–O_2 was reproducible at pH < 7 and in strongly alkaline solution only. The decay of As(IV)–O_2 was studied at pH varying from 5.4 to 5.9 in solutions containing phosphate buffer in concentrations varying from 1 × 10^{-2} to 3 × 10^{-2} mol dm^{-3}. The rate of decay was found to depend on pH only. k_{35b} was determined from measurements of the rate of formation of O_2^- in solutions containing NaOH in concentrations varying from 0.05 to 0.3 mol dm^{-3}.

The decay of O_2^- at pH = 6.9 and 10.8 was studied by the stopped-flow technique.[14] No change in the rate of decay of O_2^- was observed by addition of 0.05 mol dm^{-3} arsenate suggesting upper limits of the rate constants for the reaction of O_2^- with $H_2AsO_4^-$ and $HAsO_4^{2-}$ of 10 dm^{-3} mol^{-1} s^{-1} and 0.05 dm^3 mol^{-1} s^{-1}, respectively.

Estimation of $\Delta_fG°_{ao}$ for As(IV) Species. Standard Gibbs energies of formation, $\Delta_fG°_{ao}$, of unstable intermediates may be evaluated from measurements of the rate constants of the forward and the reverse reaction of a radical with a stable species.[39,40] By this method $\Delta_fG°_{ao}$ has been determined for OH,[39,40] Tl(II),[22] Se(V),[12] I_2^-,[10] I(VI),[7] and Xe(VII).[41] Since no such reactions were observed in the present investigation, only upper and lower limits for $\Delta_fG°_{ao}$ of the As(IV) species may be estimated. Using the values determined above for pK_6, pK_7, and pK_{12}, published values for the standard reduction potential of O_2/O_2^- and $CO_3^{\bullet-}/CO_3^{2-}$,[24] and tabulated values[42] for $\Delta_fG°_{ao}$ of the remaining relevant species, we may estimate lower limits for $\Delta_fG°_{ao}$ of As(IV) species by assuming that an upper limit for the reverse of reactions 33 and 35 are 10 dm^3 mol^{-1} s^{-1} and upper limits for $\Delta_fG°_{ao}$ of the As(IV) species by using the observation that $\Delta_fG°_{ao}$ < 0 for reaction 20.

The estimates of upper and lower limits for $\Delta_fG°_{ao}$ of the As(IV) species differ by 120 kJ mol^{-1}. The means of the upper and the lower limits of $\Delta_fG°_{ao}$ of $As(OH)_4$, $As(OH)_3O^-$ and $HAsO_3^-$, and AsO_3^{2-} are −640, −600, and −380 kJ mol^{-1}, respectively. The corresponding estimates of the standard reduction potentials

$$\text{As(OH)}_4 + \text{e}^- + \text{H}^+ \rightarrow \text{As(OH)}_3 + \text{H}_2\text{O} \tag{36}$$

$$\text{H}_3\text{AsO}_4 + \text{e}^- + \text{H}^+ \rightarrow \text{As(OH)}_4 \tag{37}$$

are +2.4 and −1.2 V, respectively. These values demonstrate that As(IV) species are both very strong oxidants and reductants.

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