Stopped-flow Study of the Reaction of $[Cr(H_2O)_6]^{3+}$ with H_3AsO_4–$H_2AsO_4^-$ and the much Faster Reaction of $[Cr(NH_3)_5(H_2O)]^{3+}$: Substitution at Arsenate(V) *

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Equilibration of $[Cr(H_2O)_6]^{3+}$ with H_3AsO_4–$H_2AsO_4^-$ to yield the 1 : 1 complex $[Cr(H_2O)_5(H_2AsO_4)]^{2+}$ has been studied in aqueous solution (I = 1.0 mol dm^{-3}, $LiClO_4$) at different temperatures with the stopped-flow technique. Results are interpreted in terms of a substitution process on the tetrahedral arsenic(V) centre leaving the Cr–O bonds intact. The corresponding reaction of $[Cr(NH_3)_5(H_2O)]^{3+}$ with H_3AsO_4–$H_2AsO_4^-$ is too fast to follow by the same method, being several orders of magnitude faster. This observation, together with the clearly negative values for the activation entropy for the process for $[Cr(H_2O)_6]^{3+}$, suggests an associatively activated mechanism for the substitution on the arsenic(V) centre.

Substitution reactions of aqua complexes of the type $[ML_5(H_2O)]^{3+}$ (L = NH_3 or H_2O; M = Cr, Co, or Rh) have been extensively studied[1–5] in order to differentiate between I_a and I_d mechanisms. Anation reactions of these complexes usually take place at the metal centre, *via* a transition state showing a greater degree of bond making with the incoming ligand than of bond breaking with the leaving ligand (I_a) or *vice versa* (I_d).[6] In this paper the kinetics and mechanism of a much less common[7,8] substitution reaction [equation (1)] are

$$[CrL_5(H_2O)]^{3+} + H_3AsO_4\text{–}H_2AsO_4^- \longrightarrow [CrL_5(H_2AsO_4)]^{2+} + H_3O^+\text{–}H_2O \quad (1)$$

studied (L = NH_3 or H_2O). This reaction, being a substitution at an inert metal centre,[9] should be slow, but is much faster than expected. Oxygen-exchange reactions for arsenic acid and $H_2AsO_4^-$ are also much faster than for the $[CrL_5(H_2O)]^{3+}$ complexes, and in view of the results obtained for similar reactions [see equation (2) where M = Cr^{III}, L = NH_3, and

$$[ML_5(H_2O)]^{3+} + X^- \longrightarrow [ML_5X]^{2+} + H_2O \quad (2)$$

X^- = IO_3^-;[10] M = Cr^{III}, L = H_2O, and X^- = IO_3^-;[11,12] or M = Co^{III}, L = NH_3, and X^- = $H_2AsO_4^-$ [9]] reaction (1) is thought to occur *via* the attack of the aqua ligand of the complex on the oxo anion. That is, in reaction (1) the metal–ligand bond remains intact and the substitution process occurs at the arsenic(V) rather than at the chromium(III) centre.

Experimental

Reagents.—Penta-ammineaquachromium(III) perchlorate was prepared from $[(NH_3)_5Cr(OH)Cr(NH_3)_5]Cl_5$, as described elsewhere.[13] The product was characterized by chromium analysis[14] and quantitative visible spectra.

Solutions of hexa-aquachromium(III) perchlorate were prepared as described in previous papers.[15] Solutions were characterized and standardized by chromium analysis and quantitative visible spectra.

Arsenic acid solutions were prepared by dissolution of the corresponding amount of $As_2O_5{\cdot}2H_2O$ (Carlo Erba RPE). The solutions were standardized by iodometry[16a] and H^+ titration using phenolphthalein (2 equivalents) or bromophenol blue (1 equivalent) as indicators.[16b]

Table 1. First two acidity constant values for arsenic acid [I = 1.0 mol dm^{-3} ($LiNO_3$)]

T/°C	10^3K_{a1}/mol dm^{-3}	10^7K_{a2}/mol dm^{-3}
5	6.17	6.92
15	5.31	6.92
25	4.17	5.25
35	3.65 *	
50	2.92	4.03

* Interpolated value from plots of ln K_{a1} *versus* $1/T$.

Other Materials.—Lithium perchlorate was prepared by addition of solid Li_2CO_3 to concentrated perchloric acid and recrystallized three times. Lithium nitrate was prepared as described elsewhere.[17] The solutions of the lithium salts were standardized by passing an aliquot down an Amberlite IR 120 (H) resin column and titrating the liberated H^+.

Stock solutions of $HClO_4$ were prepared from 60% $HClO_4$ and standardized by H^+ titration. All chemicals were reagent grade and were used without further purification.

Determination of the Acid Dissociation Constants of H_3AsO_4.—Solutions of H_3AsO_4 (5 × 10^{-2} mol dm^{-3}) were adjusted to I = 1.0 mol dm^{-3} with $LiNO_3$ ($LiClO_4$–$HClO_4$ systems gave erratic measurements as described elsewhere[17]) and titrated potentiometrically (pH meter Crison 2002) with 1.0 mol dm^{-3} NaOH until two equivalence points were observed in the neutralization curve. The experiments were run at 5, 15, 25, and 50 °C. Results are shown in Table 1, together with the value (interpolated from plots of ln K_a *versus* $1/T$) at 35 °C.

Kinetic Runs.—These were followed spectrophotometrically on a Durrum D-110 stopped-flow instrument. Runs were carried out under pseudo-first-order conditions with an excess (at least ten-fold) of total arsenic over chromium complex. When the absorbance *versus* time traces were clearly monophasic a standard first-order treatment was used. At higher temperatures and arsenic concentrations secondary reactions started to interfere, and the infinity reading had to be estimated in order to determine the $k_{obs.}$ value. In some cases,

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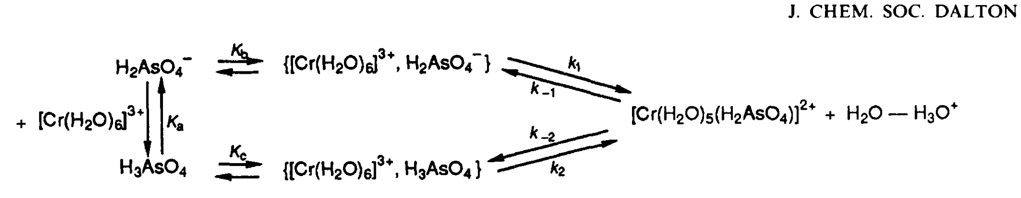
* *Non-S.I. unit employed:* cal = 4.184 J.



(3)

Guggenheim plots were also used; the results were the same, within experimental error, as those found with the A_∞ estimation. Least-square errors for the rate constants were always within 5—15% of the calculated values.

Treatment of Data.—All data were treated by the standard kinetic software included on a HP8452A spectrophotometer. Non-weighted least-square fits were used for the hyperbolic and parabolic fits.

Results

$[Cr(H_2O)_6]^{3+}$.—A good retention of isosbestic points (Figure 1) was observed for reactions of hexa-aquachromium(III) with slight excesses ([Cr]:[As] from 1:1 to 1:20) of total arsenic ($H_3AsO_4 + H_2AsO_4^-$). This rules out the possible formation of a bis or a chelated complex; only two species are present in the reaction mixture. On the other hand, the absorbance *versus* time traces indicate, again, that no consecutive reactions are observed under the conditions of the experiments. Arsenic acid acidity constants, acidity constants of similar arsenatocobalt complexes,[9] the range of pH used in this work, and the well known fact that the acidity of oxo anions is enhanced upon co-ordination lead us to consider $[Cr(H_2O)_5(H_2AsO_4)]^{2+}$ as the final product and that the only reaction occurring is that shown in equation (1). With larger excesses of the entering ligand, the isosbestic points were slowly lost, but the absorbance in the region between 490 and 450 nm remained invariant. Accordingly, reactions were followed at 475 nm, where a considerable difference in absorbance was observed between $[Cr(H_2O)_6]^{3+}$ and the final product.

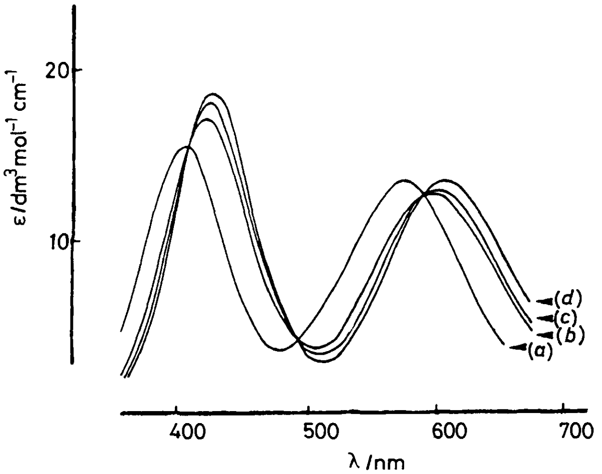


Figure 1. Superimposed visible spectra of $[Cr(H_2O)_6]^{3+}$ ($[H^+] = 0.2$ mol dm^{-3}) (*a*), and those of the final product of the reaction of $[Cr(H_2O)_6]^{3+}$ with the system H_3AsO_4–$H_2AsO_4^-$; $[As]_T$:[Cr] = 2:1 (*b*), 5:1 (*c*), and 15:1 (*d*) [room temperature, I = 1.0 mol dm^{-3} ($LiClO_4$)]

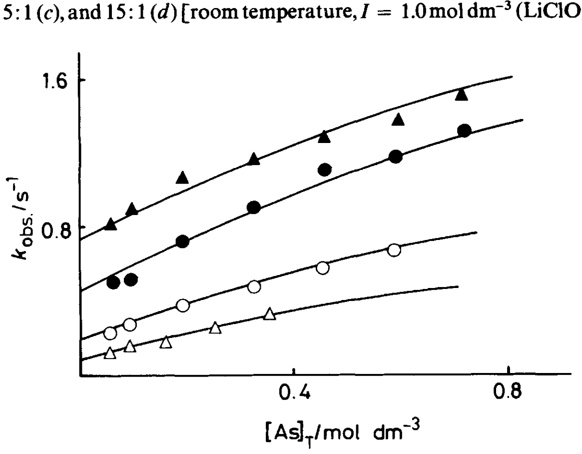


Figure 2. Plots of $k_{obs.}$ *versus* $[As]_T$ for the reaction of $[Cr(H_2O)_6]^{3+}$ with H_3AsO_4–$H_2AsO_4^-$ at different acidities; $[H^+]$ = 0.60 (▲), 0.40 (●), 0.18 (○), and 0.05 mol dm^{-3} (△) [T = 25 °C, I = 1.0 mol dm^{-3} ($LiClO_4$)]

First-order rate constants, $k_{obs.}$ (Table 2), gave a hyperbolic dependence on the total arsenic concentration at each acidity. Figure 2 shows this dependence, as well as the contribution of the back reaction to the observed rate constant. Reaction scheme (3) and the associated rate equation (4) for pseudo-first-order conditions were found to be, in principle, consistent with the rate data

$$k_{obs.} = \frac{A[As]_T}{[H^+] + K_a + B[As]_T} + C \qquad (4)$$

($[As]_T = [H_3AsO_4] + [H_2AsO_4^-]$; $A = k_1K_bK_a + k_2K_c[H^+]$, $B = K_aK_b + K_c[H^+]$, and $C = k_{-1} + k_{-2}[H^+]$. From a least-squares fit of equation (4), A, B, and C were determined at each acidity. Errors in these parameters were typically 15—20% for A, 30—40% for B, and 20—25% for C but in extreme cases they could reach 70—80% for small values (B especially). Given the fact that these values (Table 3 and Figure 3) show a non-linear dependence on $[H^+]$, reaction scheme (3) had to be changed to that shown in (5). The rate law derived from (5) is similar to that of reaction scheme (3), equation (4), but now the $[H^+]$ dependence of A, B, and C is given by $A = k_1K_aK_b + k_2K_c[H^+] + k_3(K_c/K_e)[H^+]^2$, $B = K_aK_b + K_c[H^+] + (K_c/K_e)[H^+]^2$, and $C = k_{-1} + k_{-2}[H^+] + k_{-3}[H^+]^2$. A least-squares adjustment of A (Figure 3), B, and C to these equations gave very good fits for k_2K_c, $k_3(K_c/K_e)$, k_{-2}, k_{-3}, and K_c/K_e (Table 4). The values of $k_1K_aK_b$, k_{-1}, K_b, and K_c could not be determined, their values being zero within experimental error.

From the temperature dependence of the first-, second-, and third-order rate constants the values of the activation parameters could be deterimined using the Eyring equation (Table 4).

$[Cr(NH_3)_5(H_2O)]^{3+}$.—At 25 °C the reaction of $[Cr(NH_3)_5(H_2O)]^{3+}$ with H_3AsO_4–$H_2AsO_4^-$ was too fast to be measured by flow techniques. When the temperature was decreased to 5 °C some of the absorbance *versus* time traces could be treated as first-order kinetics. Nevertheless, the values obtained for $k_{obs.}$ were erratic and no $[As]_T$ dependence could be worked out. Since the $k_{obs.}$ values were very close to the limit of the flow technique these traces were assigned to some kind of instrument artifact.

Discussion

Rate constant values obtained for this study clearly indicate that reaction (1) is much faster (at least five orders of magnitude)

Table 2. Observed rate constants ($k_{obs.}$) for the reaction of $[Cr(H_2O)_6]^{3+}$ with the system H_3AsO_4–$H_2AsO_4^-$ [I = 1.0 mol dm^{-3} ($LiClO_4$)]

T/°C	$[H^+]$/mol dm^{-3}	$[As]_T$/ mol dm^{-3}	$k_{obs.}$/s^{-1}
5	0.05	0.065	0.0205
		0.097	0.028
		0.163	0.043
		0.260	0.045
		0.358	0.065
	0.07	0.065	0.036
		0.163	0.064
		0.260	0.080
		0.358	0.112
		0.455	0.137
		0.585	0.161
	0.18	0.065	0.075
		0.097	0.105
		0.325	0.175
		0.585	0.255
	0.35	0.065	0.137
		0.097	0.140
		0.195	0.197
		0.455	0.295
		0.585	0.35
		0.715	0.38
	0.45	0.065	0.192
		0.097	0.226
		0.195	0.250
		0.325	0.34
		0.455	0.35
		0.585	0.39
		0.715	0.46
	0.60	0.065	0.275
		0.097	0.290
		0.325	0.40
		0.455	0.44
		0.585	0.50
		0.715	0.53
25	0.05	0.065	0.096
		0.097	0.123
		0.163	0.180
		0.260	0.256
		0.358	0.33
	0.07	0.065	0.125
		0.097	0.162
		0.163	0.241
		0.325	0.35
		0.455	0.51
		0.585	0.56
	0.10	0.065	0.155
		0.097	0.188
		0.195	0.285
		0.325	0.32
		0.455	0.43
		0.585	0.48
	0.18	0.065	0.225
		0.097	0.280
		0.195	0.38
		0.325	0.49
		0.455	0.58
		0.585	0.68
	0.25	0.065	0.296
		0.097	0.33
		0.195	0.46
		0.325	0.59
		0.455	0.76
		0.585	0.84
	0.35	0.065	0.44
		0.097	0.49
		0.195	0.61
		0.325	0.79
		0.455	0.85
		0.585	1.00
	0.40	0.065	0.51
		0.097	0.53
		0.195	0.71
		0.325	0.90
		0.455	1.14
		0.585	1.20
		0.715	1.34
	0.50	0.065	0.65
		0.097	0.71
		0.195	0.85
		0.325	1.03
		0.455	1.14
		0.585	1.26
		0.715	1.31
	0.60	0.065	0.81
		0.097	0.89
		0.195	1.07
		0.325	1.18
		0.455	1.29
		0.585	1.38
		0.715	1.49
35	0.05	0.065	0.30
		0.097	0.38
		0.195	0.83
		0.325	1.09
		0.455	1.56
		0.585	1.84
	0.07	0.065	0.36
		0.097	0.49
		0.195	0.82
		0.390	1.52
		0.585	2.01
	0.18	0.065	0.52
		0.097	0.64
		0.195	1.07
		0.390	1.66
		0.585	2.20
	0.35	0.065	1.10
		0.097	1.29
		0.195	1.83
		0.390	2.63
		0.585	3.35
	0.45	0.065	1.32
		0.097	1.55
		0.195	2.00
		0.390	2.66
		0.585	3.00

than that with the equivalent phosphorus(V) system (H_3PO_4–$H_2PO_4^-$).[15,18] These results are in good agreement with a substitution reaction at a labile arsenic(V) centre *versus* one at an inert chromium(III) centre. Given the fact that for water-exchange reactions the rate increases in the order $H_3PO_4 < [Cr(H_2O)_6]^{3+} \ll H_3AsO_4$, reaction of hexa-aquachromium(III) with the phosphorus system has to proceed *via* a Cr–O bond breakage,[19] but the reaction of the same complex with the H_3AsO_4–$H_2AsO_4^-$ system has to go *via* an As–O bond-breaking[9] process. For the reaction studied in this paper, an associatively activated mechanism is proposed, with an intermediate of type (A), as has already been done for studies with other labile oxo anions (IO_3^-, $HSeO_3^-$, *etc.*).[9–12,20] This associatively activated mechanism is also supported by the

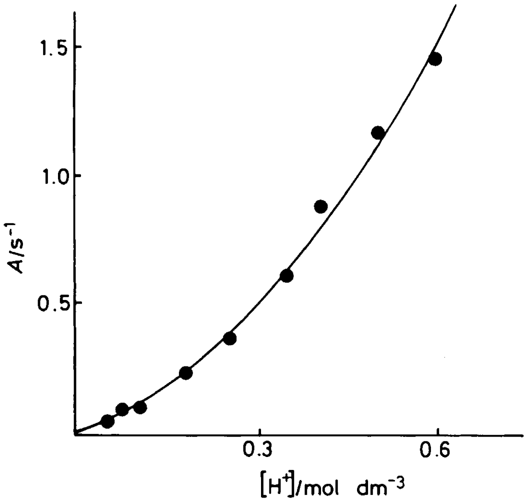
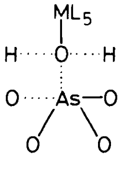


Figure 3. Parabolic fit of the dependence of A versus $[H^+]$ at 25 °C $[I = 1.0\ \mathrm{mol\ dm^{-3}}\ (LiClO_4)]$; (——), mathematically adjusted curve

Table 3. Values for the parameters A, B, and C [equation (4)] for the reaction of $[Cr(H_2O)_6]^{3+}$ with the system H_3AsO_4–$H_2AsO_4^-$ $[I = 1.0\ \mathrm{mol\ dm^{-3}}\ (LiClO_4)]$

T/°C	$[H^+]$/ mol dm^{-3}	A/s^{-1}	B	C/s^{-1}
5	0.05	0.011	0.055	0.010
	0.07	0.021	0.018	0.019
	0.18	0.081	0.089	0.055
	0.35	0.17	0.12	0.11
	0.45	0.22	0.14	0.17
	0.60	0.35	0.32	0.24
25	0.05	0.051	0.023	0.037
	0.07	0.091	0.047	0.050
	0.10	0.097	0.078	0.10
	0.18	0.24	0.14	0.15
	0.25	0.36	0.13	0.20
	0.35	0.61	0.35	0.34
	0.40	0.89	0.34	0.36
	0.50	1.2	0.73	0.51
	0.60	1.5	1.0	0.68
35	0.05	0.22	0.030	0.038
	0.07	0.32	0.041	0.079
	0.18	0.89	0.14	0.22
	0.35	2.8	0.43	0.61
	0.45	3.8	0.99	0.86



(A)

clearly negative activation entropy values shown in Table 4 and by the large difference in reactivity on changing the entering species $\{[CrL_5(H_2O)]^{3+}, L = H_2O \text{ or } NH_3\}$.

This difference in the reactivity has to be related to the electronic factors arising from the substitution of five H_2O by five NH_3 in the co-ordination sphere of chromium(III). The presence of NH_3 groups rather than H_2O increases the electron density on the chromium(III) centre and thus on the oxygen of the aqua ligand attached, as shown by the pK_a values for the two complexes ($L = NH_3$, $pK_a = 5.0$; $L = H_2O$, $pK_a = 4.1$, 25 °C).[21,22] As a result, this oxygen will react more easily with the arsenic centre. The steric effect due to NH_3 being larger than H_2O must be negligible, as expected for a reaction with a transition state as in (**A**), where the steric hindrance due to the L ligands occurs at the chromium(III) centre and not on the 'attacked' arsenic centre.

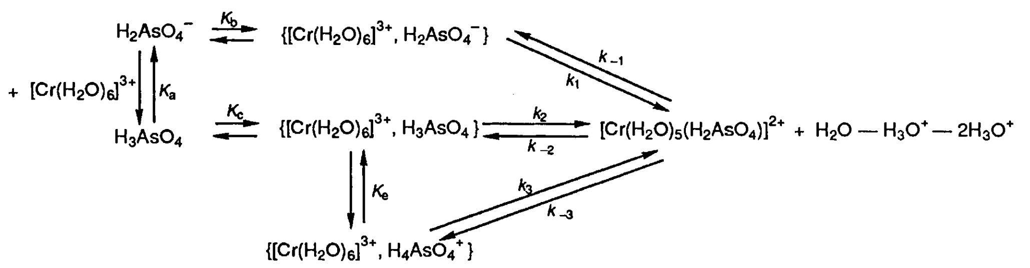
With respect to the proposed reaction scheme (5), there are three features to be considered:

(*i*) The existence of the outer-sphere complex, $\{[Cr(H_2O)_6]^{3+}, H_4AsO_4^+\}$, arising from protonation of $\{[Cr(H_2O)_6]^{3+}, H_3AsO_4\}$. This protonation could be explained by considering some sort of interaction between the chromium(III) complex and the anating species (H_3AsO_4) in the outer-sphere complex $\{[Cr(H_2O)_6]^{3+}, H_3AsO_4\}$, as has already been considered in other associatively activated substitution reactions of Cr^{III}.[2,18] In this way, further electron enrichment of the arsenic-bound oxygens is achieved, and $\{[Cr(H_2O)_6]^{3+}, H_3AsO_4\}$ becomes more easily protonated than the corresponding free arsenic acid. This protonation could be of the same type as that detected in the acid catalyses for the oxygen-exchange reactions of labile oxo anions.[23]

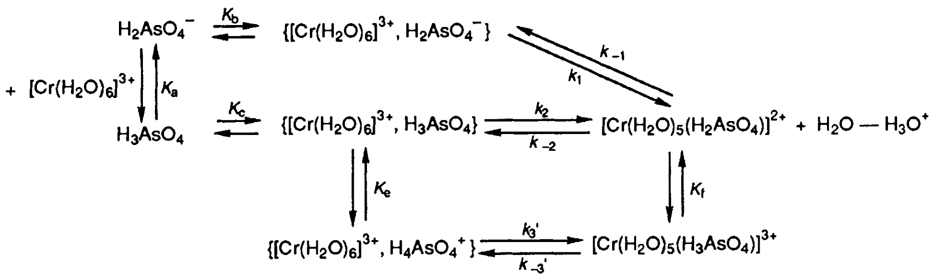
(*ii*) A termolecular elementary step in reaction scheme (5) is represented by k_{-3}. Statistically, this step has a very small probability of occurrence. If the species $[Cr(H_2O)_5(H_3AsO_4)]^{3+}$ is postulated $\{[Co(NH_3)_5(H_3AsO_4)]^{3+}$ has been reported[9]$\}$ and its concentration kept low in a steady state, the following reaction scheme (6) could be considered. This new

Table 4. Summary of rate constants, activation parameters, and equilibrium constants corresponding to reaction scheme (5) $[I = 1.0\ \mathrm{mol\ dm^{-3}}\ (LiClO_4)]$

T/°C	K_c/K_e	$k_3(K_c/K_e)$/s^{-1}	K_ck_2/dm^3 mol^{-1} s^{-1}	k_3/s^{-1}	k_{-2}/dm^3 mol^{-1} s^{-1}	k_{-3}/dm^6 mol^{-2} s^{-1}
5	$(8.7 \pm 1.0) \times 10^{-1}$	$(3.2 \pm 1.3) \times 10^{-1}$	$(3.9 \pm 0.8) \times 10^{-1}$	$(3.7 \pm 2.0) \times 10^{-1}$	$(2.2 \pm 0.6) \times 10^{-1}$	$(2.9 \pm 0.9) \times 10^{-1}$
25	2.8 ± 0.5	2.3 ± 0.6	1.1 ± 0.4	$(8.2 \pm 4.0) \times 10^{-1}$	$(5.1 \pm 1.3) \times 10^{-1}$	$(9.6 \pm 2.1) \times 10^{-1}$
35	4.5 ± 0.3	$(1.1 \pm 0.4) \times 10^{1}$	3.9 ± 2.2	2.4 ± 1.0	$(9.2 \pm 2.2) \times 10^{-1}$	2.3 ± 0.4
$\Delta H^{\ddagger}$(kcal mol^{-1})			12 ± 3	9.5 ± 3.1	7.4 ± 0.9	11 ± 1
$\Delta S^{\ddagger}$(cal K^{-1} mol^{-1})			$-18 + 7$	-26 ± 13	-35 ± 8	-22 ± 3



(5)



(6)

scheme (6) is kinetically indistinguishable from (5), and now $k_{-3'}$ represents a more likely bimolecular step ($k_{-3} = k_{-3'}/K_f$).

(*iii*) Finally, we have not been able to detect rate constants k_1 and k_{-1}. This is probably due both to their small relative values (when compared with k_2 or k_3, and k_{-2} or k_{-3}) and to the fact that, under the experimental conditions used, $[H_2AsO_4^-]/[H_3AsO_4]$ had a maximum value of 0.1.

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