Kinetics of an Associative Ligand Exchange Process: Alcohol Exchange with Arsenate(v) and Vanadate(v) Esters

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Summary Alcohol exchange with trialkyl arsenates and vanadates is rapid and appears to proceed *via* a 5-co-ordinate transition state wherein the degree of bond-breaking is governed by the steric size of the alkyl group.

Unlike phosphate esters, which are relatively stable, arsenate(v) and vanadate(v) esters are known to be labile with respect to hydrolysis[1] or alcohol exchange.[2] However, solvolysis of these esters has received no detailed kinetic study. We report an investigation by ^{1}H n.m.r. line broadening of the kinetics of the degenerate alcohol exchange reactions of the esters $(RO)_3AsO$, where R = Et, Pr^n, Bu^n, or Pe^n, and $(RO)_3VO$, where R = Pr^n, Pr^i, Bu^n, or Pe^n (Pe^n = n-pentyl).

Table 1

$VO(OR)_3$ chemical shifts and rate parameters

R	δ^{a,b}	τ_A/s^b	$\Delta H^\ddagger$/kJ mol^{-1}	$\Delta S^\ddagger$/J mol^{-1} K^{-1}
Pr^n	4.95	0·062	21·4 ± 1·2	−150 ± 9
Bu^n	—	0·057	22·4 ± 0·9	−146 ± 3
Pe^n	5·00	0·110	26·4 ± 1·5	−138 ± 8
Pr^i	5·14	0·97	32·7 ± 3·0	−129 ± 9

[a] p.p.m. from Me_4Si. [b] At 25 °C.

The esters were prepared by the reaction of Ag_3AsO_4 with RBr,[3] or by the reaction of NH_4VO_3 with ROH.[4] Chemical shifts of the ester α-methylene protons, measured at 60 MHz, are given in Tables 1 and 2. The $(EtO)_3AsO$ value is in good agreement with the result of Durand and Laurent;[5] the $(Pr^nO)_3VO$ and $(Bu^nO)_3VO$ shifts are consistent with those recently reported by Lachowitz, *et al.*,[6] but the shifts reported[6] for $(Pe^nO)_3VO$ and $(Pr^iO)_3VO$ are inexplicably large. The vanadate ester chemical shifts are temperature dependent (−0·0019 p.p.m. K^{-1} for the straight-chain esters, −0·00065 for the Pr^i ester), possibly reflecting a variation in the degree of intermolecular association.[6]

Spectra of $(RO)_3VO$–ROH mixtures show separate α-proton multiplets at room temperature and below. With increasing temperature, the multiplets broaden, and their positions approach one another, eventually approaching coalescence. Spectra were analysed by comparison with computer-simulated spectra to obtain τ_A, the lifetime of the α-protons in the alcohol environment (since a 1:3 mole ratio was used, lifetimes in the alcohol and ester environments were equal.) Chemical shifts and relaxation times, used to compute the simulated spectra, were estimated from lower temperature results and/or from spectra of the neat components. Exchange lifetimes, extrapolated to 25 °C, are given in Table 1, together with the activation parameters, $\Delta H^\ddagger$ and $\Delta S^\ddagger$, for the exchange process.

The activation parameters given in Table 1 indicate a transition state involving little bond-breaking, but with substantial loss of entropy, suggesting an associative exchange process. $\Delta H^\ddagger$ increases with the size of the alkyl group, whilst $\Delta S^\ddagger$ becomes less negative; thus as the steric requirements become more stringent, the reaction mechanism apparently changes towards a displacement process with a greater degree of bond-breaking in the transition state.

Table 2

$AsO(OR)_3$ chemical shifts and rate contants^a

R	δ^b	k_2/l mol^{-1} s^{-1}	k_3/l^2 mol^{-2} s^{-1}
Et	4·08	6·9 ± 2·6	125 ± 19
Pr^n	4·02	8·2 ± 1·0	61 ± 7
Bu^n	4·07	5·3 ± 1·6	75 ± 11
Pe^n	4·04	7·2 ± 1·6	71 ± 12

[a] At 66 °C in acetonitrile. [b] p.p.m. from Me_4Si.

Alcohol exchange with both $(RO)_3VO$ and $(RO)_3AsO$ is catalysed by toluene-*p*-sulphonic acid. Small amounts of catalyst cause complete coalescence of the α-proton resonances in $(RO)_3VO$–ROH mixtures. Exchange in the $(RO)_3AsO$–ROH system, however, must be catalysed in order that the rate be measureable. Values of τ_A^{-1}, determined from spectra of acetonitrile solutions of $(RO)_3AsO$, ROH, and catalyst at 66 °C, are linear in $[C_7H_7SO_3H]$, and the uncatalysed rate can be found by extrapolation. Preliminary experiments, in which $[(RO)_3AsO]$ and [ROH] were varied, gave results consistent with a reaction first-order in both ester and alcohol. τ_A^{-1} may be related to second- and third-order rate constants for the uncatalysed and catalysed reactions, respectively: $\tau_A^{-1} = \{k_2 + k_3[C_7H_7SO_3H]\}[ROH]$. The rate constants k_2 and k_3 are given in Table 2. Except for the more rapid catalytic exchange of ethyl groups, the results for the other alkyl groups are not easily distinguished. The activation parameters should be more revealing. Preliminary results for the acid-catalysed $(Bu^nO)_3AsO$–Bu^nOH exchange suggest $\Delta H^\ddagger$ = *ca.* 14 kJ mol^{-1} and $\Delta S^\ddagger$ = *ca.* −180 J mol^{-1} K^{-1}.

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