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Kinetics of substitution at the metallocene dichlorides $M(\eta^5\text{-}C_5H_5)_2Cl_2$ (M = Ti or V) in acetonitrile

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Abstract

The rate law and rate constants are reported for substitution in bis-cyclopentadienyltitanium(IV) dichloride by bromide, iodide, thiocyanate, and cyanide, and at the vanadium(IV) and bis-pentamethylcyclopentadienyl analogues by thiocyanate, in acetonitrile solution. The effects on reactivities of the addition of small amounts of water or of toluene are described, and considered in terms of changes in solvation.

Introduction

A few years after the characterisation of titanium, vanadium, and zirconium cyclopentadienyl halides of the $M(cp)_2X_2$ $\{cp = \eta^5\text{-}C_5H_5\}$ type [1], Jensen and Basolo investigated kinetics of substitution in complexes $Ti(cp)_2X_2$ by monitoring the replacement of Br^- by Cl^- in benzene and in THF [2]. Jensen [3] and Langford and Aplington [4] studied further reactions of this type in acetone. Recent indications of therapeutic value of dichloro-cyclopentadienyl complexes $M(cp)_2Cl_2$ (M = Ti, V, or Zr) [5] led to a study of their equilibrium and kinetic properties in aqueous media [6]. There has also been a recent report on kinetics of redistribution reactions of a series of compounds $Zr(cp)_2X_2$ with X = halide, methyl, or phenyl [7]. We have studied the kinetics of chloride replacement in $Ti(cp)_2Cl_2$ and, briefly, its C_5Me_5 and vanadium analogues in acetonitrile solution.

Experimental

The dichloro complexes $Ti(cp)_2Cl_2$ [1], $Ti(Me_5cp)_2Cl_2$ [8], $V(cp)_2Cl_2$ [1], and $Zr(cp)_2Cl_2$ [1] were prepared by standard procedures. $Ti(cp)_2Br_2$ and $Ti(cp)_2(NCS)_2$

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(needed for product characterisation by spectroscopy) were prepared from $Ti(cp)_2Cl_2$ by metathesis involving use of lithium bromide or thiocyanate in acetonitrile. Each of these compounds gave satisfactory C, H, and N analyses; the ultraviolet-visible spectra of their solutions were consistent with published data [9]. The kinetic runs were carried out with acetonitrile solutions of potassium thiocyanate, lithium bromide, lithium iodide, or tetraethylammonium cyanide. The first three of these were AnalaR grade; the last-named was used as received (Fluka).

Kinetics were monitored spectrophotometrically, in 10 mm silica cells in the thermostatted cell compartment of a Hewlett Packard HP8451 instrument [10]. Preliminary runs with $V(cp)_2Cl_2$ were carried out with ESR monitoring, but poor thermostatting of the sample precluded use of this method for measurement of accurate rate constants.

Results and discussion

Rate law and mechanism

Replacement of the two chlorides in $Ti(cp)_2Cl_2$ by entering groups such as thiocyanate, iodide, bromide, or cyanide takes place in only one observable kinetic step. Repeat scan spectra show clean isosbestic points, e.g. at 368 and 406 nm for the reaction with bromide. When the initial concentration of the incoming group is very much larger than that of the titanium compound, first-order kinetics are obeyed for at least three half-lives; there is no sign of consecutive reactions nor of the transient existence of species $Ti(cp)_2ClX$. Our results are analogous to those described by Jensen and Basolo [2]. The rate-limiting step is the loss of the first chloride from $Ti(cp)_2Cl_2$. Table 1 and Fig. 1 show how first-order rate constants ($[\text{nucleophile}] \gg [Ti(cp)_2Cl_2]$) vary with the nature and concentration of four anionic entering groups in acetonitrile solution at 298.2 K. The rate law indicated is

$$+\mathrm{d}\{Ti(cp)_2X_2\}/\mathrm{d}t = \{k_1 + k_2[X]\}[Ti(cp)_2Cl_2]$$

The value of k_1 is independent of the nature of the incoming anion (Table 1). This rate law suggests parallel dissociative (k_1) and associative (k_2) paths. The order of k_2 values (Table 1), which increase with variation of the anion in the sequence $Br^- < I^- < NCS^- < CN^-$, seems reasonable for a "hard" titanium(IV) centre which has been very much "softened" by the coordination of two cyclopentadienyl groups (cf. "hard" Co^{3+} but "soft" $[Co(CN)_5]^{2-}$). Associative substitution has been suggested for some other titanium(IV) complexes; for example, chloride exchange in

Table 1

Observed first-order rate constants and derived values of k_1 and k_2 (cf. rate law in text) for reaction of $Ti(cp)_2Cl_2$ with nucleophiles in acetonitrile solution at 298.2 K: initial $[Ti(cp)_2Cl_2] = 10^{-4}$ mol dm^{-3}

	10^3k_{obs} (s^{-1})							10^3k_1 (s^{-1})	k_2 (M^{-1} s^{-1})
[nucl] (M^{-1})	0.01	0.03	0.05	0.08	0.10	0.15	0.20		
Br^-		2.6	2.7		2.9	3.4	3.8	2.5	0.012
I^-		3.3	3.6		4.0	4.9	5.4	2.7	0.026
NCS^-	3.9	8.5	12.8	19.6	23.2	33	40	2.5	0.203
CN^-	~14								~14

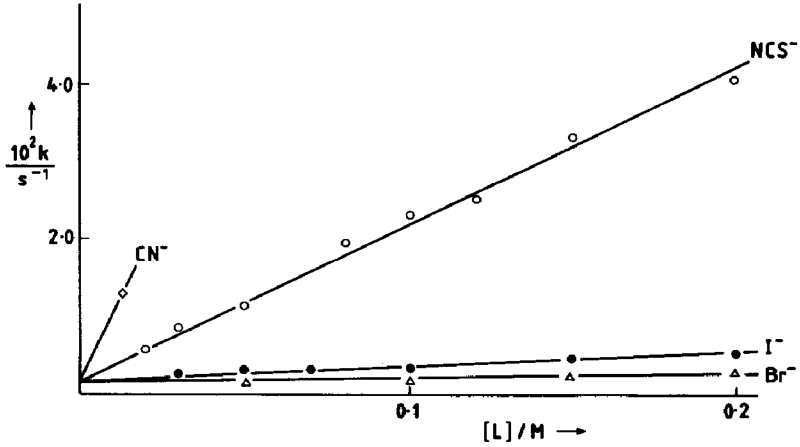

Fig. 1. Dependence of observed first-order rate constants on nucleophile concentration for substitution at $Ti(cp)_2Cl_2$ in acetonitrile at 298.2 K.

the pentane-1,2-dione derivative $Ti(acac)_2Cl_2$ [11]. In this case both the rate law and the activation entropy indicated associative attack by the incoming chloride. Associative attack at titanium(IV) has also been proposed in the reaction of Ti^{IV}-porphyrin with hydrogen peroxide [12]; dissociative reactions of cyclopentadienyltitanium compounds include that of substitution at $Ti(cp)_2(CO)_2$, though it must be said that this latter system involves Ti^{II} and is photochemically activated [13].

Non-leaving ligand effects

The replacement of cp by its pentamethyl derivative results in a marked decrease in reactivity (Table 2). Electron release by the methyl groups makes formation of the incipient bond to the entering group more difficult (smaller k_2). It also seems to strengthen the metal–chloride bonding somewhat, since k_1 is also slightly decreased.

Effect of central metal

$V(cp)_2Cl_2$ reacts considerably more slowly than $Ti(cp)_2Cl_2$ (Table 2). This difference may be ascribed to crystal field effects; titanium(IV) is d^0, vanadium(IV) is d^1 – only the latter has crystal field stabilisation. The vanadium compound reacts predominantly by the associative pathway – compare the associative nature of

Table 2

Observed first-order rate constants and derived values of k_1 and k_2 (cf. rate law in text) for reaction of $Ti(Me_5cp)_2Cl_2$ and of $V(cp)_2Cl_2$ with thiocyanate in acetonitrile solution at 298.2 K: initial [complex] = 10^{-4} mol dm^{-3}

$[MCS^-]/(M^{-1})$	10^3k_{obs} (s^{-1})						10^3k_1 (s^{-1})	k_2 $(M^{-1}$ $s^{-1})$
	0.01	0.03	0.05	0.10	0.15	0.20		
$Ti(Me_5cp)_2Cl_2$	1.5	2.4	4.2	6.9	9.4	11.3	1.2	0.053
$V(cp)_2Cl_2$			0.58	1.03	1.6	2.1	~ 0.1	0.00010
cf. $Ti(cp)_2Cl_2$							2.5 [a]	0.203 [a]

[a] From Table 1.

Table 3

Observed first-order rate constants and derived values of k_1 and k_2 (cf. rate law in text) for reaction of $Ti(cp)_2Cl_2$ with thiocyanate in acetonitrile/water and acetonitrile/toluene media at 298.2 K: initial [complex] $= 10^{-4}$ mol dm^{-3}

	10^3k_{obs} (s^{-1})								10^3k_1 (s^{-1})	k_2 (M^{-1} s^{-1})
[NCS$^-$]/(M^{-1})	0.01	0.02	0.03	0.04	0.05	0.08	0.10	0.15		
added water [a]										
1%	4.3		8.6		11.5	17.1	20.9	27.7	3.3	0.17
3%	9.7		12.7		17.2	21.3	23.9		8.5	0.16
5%	18.5	20.8	21.5	22.5	24.1		31.8		17.2	0.14
added toluene [a]										
5%	3.9		8.7		13.9	22.1	25.7	40.7	0.9	0.26
10%	3.9		7.2 [b]		15.0	25.7	33.7		0	0.33

[a] Volume per cent before mixing. [b] [NCS$^-$] = 0.025 mol dm^{-3}.

dimethyl sulphoxide exchange at the $[VO(dmso)_5]^{2+}$ cation, established by determination of the activation volume for this process [14]. Unfortunately it proved impossible to study kinetics of substitution at $Zr(cp)_2Cl_2$ in acetonitrile owing to the development of cloudiness soon after the start of reaction.

Solvent effects

The effects of making relatively small changes to the medium by adding up to 5% of water or 10% of toluene to the acetonitrile have been established for the reaction of $Ti(cp)_2Cl_2$ with thiocyanate (Table 3). The trends in the rate constants k_1 and k_2 are illustrated in Fig. 2.

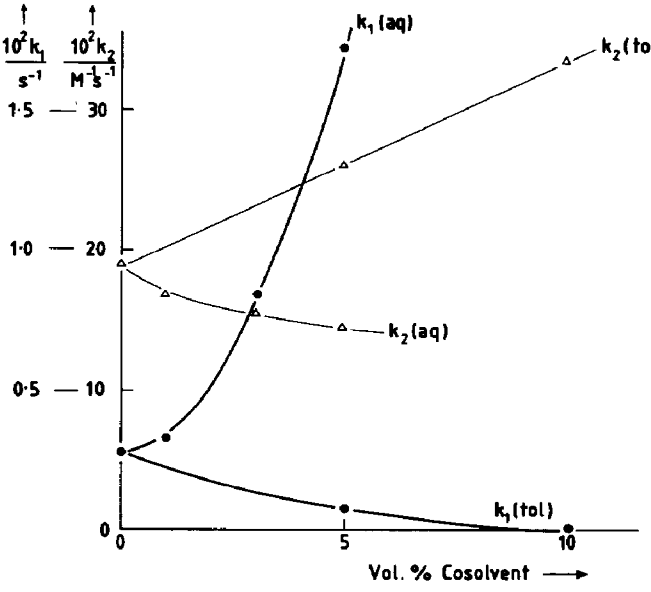

Fig. 2. Dependence of derived first- and second-order rate constants for reaction of $Ti(cp)_2Cl_2$ with thiocyanate on solvent composition for acetonitrile containing small amounts of water (aq) or toluene (tol).

As the water content increases k_1 increases rapidly. This may be ascribed to increasingly favourable solvation of leaving chloride; the transfer chemical potential of chloride from acetonitrile to acetonitrile containing 10% water is greater than -18 kJ mol^{-1} [15]. Addition of 5% water leads to a six-fold increase in rate constant, an effect rather similar to that of the addition of 5% water to ethanol in solvolysis of t-butyl chloride [16]. The small but significant decrease in k_2 suggests that desolvation of the incoming group is slightly more important than solvation of leaving chloride in this S_N2 path, or, in other words, that bond-making is rather more important than bond-breaking in transition state formation.

As toluene is added k_1 decreases, effectively reaching zero by the time 10% toluene has been reached. This trend is compatible with Jensen and Basolo's observations on the reaction of $Ti(cp)_2Br_2$ with chloride in benzene, for which no k_1 term was perceived [2]. Such behaviour is consistent with decreasing solvation assistance to the leaving chloride. The increase in k_2 as the percentage of toluene increases presumably reflects the chemical potential of the thiocyanate increasing more than that of the leaving chloride. Again bond-making appears to dominate over bond-breaking .

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