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Kinetic Studies on the Complexing of Aquo TiO^{2+} with Thiocyanate, Pyrophosphate, and Hydrogen Fluoride

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The 1:1 equilibration of NCS^- with TiO^{2+} has been studied by the temperature-jump technique. With NCS^- in large excess reciprocal relaxation times fit a dependence $\tau^{-1} = k_f[NCS^-] + k_b$. At 25 °C, $I = 0.50$ M ($LiClO_4$), rate constants and activation parameters ($\Delta H^{\ddagger}$, kcal mol^{-1}; $\Delta S^{\ddagger}$, cal K^{-1} mol^{-1}) for the forward and back reactions respectively are $k_f = 2.21 \times 10^3$ M^{-1} s^{-1} (11.7, -4.0) and $k_b = 7.2 \times 10^2$ s^{-1} (14.9, 4.6). Only the forward reaction is observed with pyrophosphate, and at 25 °C (stopped-flow) rate constants for 1:1 complexation are 1.10×10^3 M^{-1} s^{-1} ($H_4P_2O_7$), 0.95×10^3 M^{-1} s^{-1} ($H_3P_2O_7^-$), and 3.60×10^3 ($H_2P_2O_7^{2-}$). Rate constants for 2:1 ligand to metal complex formation were also obtained. The forward reaction is predominant in the reaction with HF, and (stopped-flow) kinetic data are $k_f = 1.86 \times 10^3$ M^{-1} s^{-1}, $\Delta H_f^{\ddagger} = 10.6$ kcal mol^{-1}, and $\Delta S^{\ddagger} = -8.0$ cal K^{-1} mol^{-1}. No pathway for complexing by F^- was detected with $[H^+] = 0.11$–0.48 M. The rate constant pattern, $I = 0.50$ M ($LiClO_4$), for the five 1:1 formation reactions of TiO^{2+} investigated strongly suggests an I_d mechanism. A similar mechanism has previously been suggested for other oxo ions VO^{2+} and $Mo_2O_4^{2+}$.

A recent investigation[1] has substantiated earlier suggestions[2,3] that the titanium(IV) aquo ion in aqueous perchloric acid solutions is TiO^{2+} and therefore to be regarded as analogous to VO^{2+}. No assessment has yet been made of the ligand substitution properties of TiO^{2+}, however, and the aim of the present work is to rectify this situation. The range of possible reactants for such studies is restricted by the absence of suitable spectrophotometric changes in the UV-visible range. It is also necessary to work at pH <2 to avoid precipitation of Ti(IV), and under these conditions some potential ligands are protonated and less reactive. Three studies have been possible, and from the rate constant pattern which emerges it is possible to comment on the mechanism of substitution.

Experimental Section

Reagents. Solutions of titanium(IV) perchlorate (ca. 0.04 M) in 1.0 M perchloric acid were prepared by the procedure as used in earlier work from these laboratories.[4] AnalaR grade ammonium thiocyanate and sodium pyrophosphate were used. Hydrogen fluoride (CARE!) was prepared from sodium fluoride and $HClO_4$ (both AnalaR), and aqueous solutions (0.6 M) were stored in plastic containers. No change in path length or etching of optical (silica) cells was observed on leaving 5×10^{-2} M HF for periods of ca. 24 h. All glassware was washed rigorously with water immediately after contact with HF. Lithium perchlorate was obtained by addition of lithium carbonate to AnalaR perchloric acid and recrystallizing two or three times.

Protonation Constants. The protonation constant for fluoride is 1.2×10^3 M^{-1} at 20 °C, $I = 1.0$ M ($NaClO_4$).[5] For the range of $[H^+]$ investigated (0.11–0.48 M) there is little formation of F^-, and association of F^- with HF to give HF_2^- is likewise small (formation constant 2.6 M^{-1}).[5] The four protonation constants for pyrophosphate are relevant to the interpretation given, and it was necessary therefore to determine these for the experimental conditions used, 25 °C, $I = 0.50$ M ($LiClO_4$). A solution (50 mL) of $Na_4P_2O_7$ (0.05 M) in $HClO_4$ (0.20 M) was made up, $I = 0.50$ M ($LiClO_4$), and titrated with NaOH (0.50 M). The pH was monitored on a Radiometer Type PHM 4d meter using G202C glass and K401 calomel electrodes, after addition of each 0.50 mL (magnetic stirring). The pH meter was calibrated using 10^{-2} M $HClO_4$, $I = 0.50$ M ($LiClO_4$). Analysis of data was carried out using the MINIQUAD computer program.[6] Satisfactory reproducibility of titration curves was obtained (individual points to <±2%). Protonation constants (K_H) obtained, Table I, are similar to literature values.[7,8] Concentrations of various $H_xP_2O_7^{(4-x)-}$ species and free $[H^+]$ were calculated from K_H values determined. Calculations necessary to enable ionic strength adjustments were made using a computer program, details of which have been reported.[9]

Formation Constants. The reactant thiocyanate absorbs at wavelengths ≤270 nm. A spectrophotometric method was used to determine the formation constant for 1:1 complexing with TiO^{2+}. At 25 °C, λ 275 nm, the absorption coefficient of TiO^{2+} is ϵ_0 80 M^{-1} cm^{-1}, and the absorbance increases on addition of thiocyanate. Conditions were $I = 0.10$ M ($LiClO_4$), with $[Ti(IV)] = 4 \times 10^{-4}$ M, $[NCS^-] = 0.03$–0.075 M, and $[H^+] = 0.025$ M. The increase in absorption coefficient $(\epsilon_{obsd} - \epsilon_0)^{-1}$ is given by $[Ti(IV)]/\Delta A$ (ΔA is the increase in absorbance on addition of NCS^-, 1-cm cell), which is related to the equilibrium constant K_T by

$$\frac{1}{\epsilon_{obsd} - \epsilon_0} = \frac{1}{K_T[NCS^-](\epsilon_1 - \epsilon_0)} + \frac{1}{\epsilon_1 - \epsilon_0} \qquad (1)$$

where ϵ_1 is the absorption coefficient for $TiO(NCS)^+$.

Table I. Protonation Constants (K_H, M^{-1}) for Pyrophosphate as Determined by pH Titration at 25 °C, $I = 0.50$ M ($LiClO_4$), and a Comparison with Literature Values in Different Solution Media

	log K_H		
Anion	0.50 M $LiClO_4$[a]	1.0 M $NaClO_4$[b]	1.0 M NMe_4Br[c]
$P_2O_7^{4-}$	7.38	7.36	8.71
$HP_2O_7^{3-}$	5.54	5.36	5.76
$H_2P_2O_7^{2-}$	1.56	1.40	1.72
$H_3P_2O_7^-$	0.798	0.75	0.79

[a] This work, standard deviation ±5%. [b] Reference 7. [c] Reference 8.

With pyrophosphate two kinetic stages corresponding to formation of 1:1 and 2:1 ligand to metal complexes were observed. Since no pyrophosphate-independent reaction was observed it was concluded that the reaction proceeded to completion in each case.

Spectrophotometric measurements (250–300 nm) indicated extensive complexing of hydrogen fluoride with TiO^{2+} for the range of conditions investigated. This was confirmed by making up solutions $[Ti(IV)] = 7.4 \times 10^{-3}$ M, $[HF] = 7.4 \times 10^{-2}$ M, and $[H^+] = 0.25$ M, with $I = 0.50$ M ($LiClO_4$), at 21 °C, and subjecting these to a 4.0 °C temperature jump (40 kV). No spectrophotometric changes accompanied the jump. Only when [HF] decreased to 1.5×10^{-2} M was a very small change in transmittance obtained. A limiting value for the formation constant was obtained from the kinetics using the stopped-flow method.

Kinetics. Temperature-jump equipment (Messanlagen-Studiengesellschaft, Göttingen) in conjunction with a Tektronics 564B storage oscilloscope was used to study the 1:1 equilibration of NCS^- with TiO^{2+}. Only a single transmittance change was observed at 272 nm. Reciprocal relaxation times (τ^{-1}) were evaluated from transmittance against time oscilloscope traces using an exponential simulator[10] and from the slope (×2.303) of plots of absorbance changes, log (ΔA), against time. Plots were linear to >80%, and results obtained by the two methods were in agreement. Initially experiments were at $I = 0.10$ M with $[Ti(IV)] = 3.94 \times 10^{-4}$ M, $[NCS^-] = 0.0125$–0.075 M, and $[H^+] = 0.025$–0.090 M. Solutions were used within 1 h of being prepared from stock solutions as Ti(IV) tends to precipitate if kept for long periods (24 h) at pH >1. Only a relatively small dependence of τ^{-1} on $[NCS^-]$ is obtained at $I = 0.10$ M, however, and to obtain greater precision the latter was increased to 0.50 M thus enabling $[NCS^-]$ to be increased. Under these conditions reactant concentrations were varied: $[Ti(IV)] = (0.5$–$1.5) \times 10^{-3}$ M, $[NCS^-]$

Table II. Reciprocal Relaxation Times (λ 275 nm) for the Equilibration of TiO^{2+} with NCS^-, $I = 0.50$ M ($LiClO_4$)

Temp, °C	$[H^+]$, M	10^3·[Ti(IV)], M	10·$[NCS^-]$, M	$10^{-2}\tau^{-1}$,[d] s^{-1}
25.0	0.30	1.5	0.225	7.7 (5)
	0.10	1.5	0.80	9.1 (4)
	0.35	1.5	1.40	9.9 (5)
	0.30	0.5	2.00	11.5 (4)
	0.19	1.5	3.00	14.2 (4)
16.1	0.30	1.5	0.225	3.45 (4)
	0.35	1.5	1.40	4.60 (4)
	0.30	0.5	2.00	5.30 (4)
	0.24	0.5	2.60	6.09 (4)
	0.19	1.5	3.00	6.34 (4)
9.7	0.30	1.5	0.225	1.83 (5)
	0.10	1.5	0.80	2.60 (4)
	0.35	1.5	1.40	3.00 (5)
	0.30	0.5	2.0	2.97 (2)
	0.30	0.5	2.0	3.06 (1)[a]
	0.30	0.5	2.0	2.90 (1)[b]
	0.30	0.5	2.0	2.94 (1)[c]
	0.20	1.5	2.8	3.69 (4)

[a] λ 285 nm. [b] λ 300 nm. [c] λ 315 nm. [d] Figures in parentheses indicate number of runs averaged.

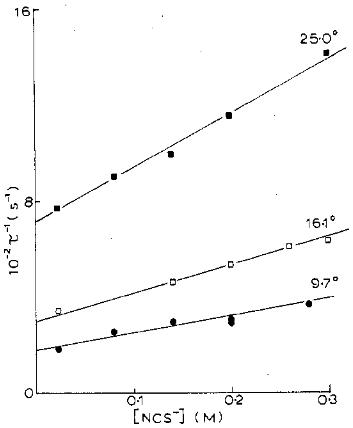

Figure 1. Plot of reciprocal relaxation time against $[NCS^-]$ for the reaction of TiO^{2+} with NCS^-, $I = 0.50$ M ($LiClO_4$).

= 0.025–0.30 M, and $[H^+] = 0.10$–0.41 M. A greater than tenfold excess of $[NCS^-]$ over [Ti(IV)] was maintained throughout.

The reaction of pyrophosphate with TiO^{2+} was monitored at 330 nm on a Durrum-Gibson stopped-flow spectrophotometer. Reactant concentrations were [Ti(IV)] = (4–20) × 10^{-4} M, $[P_2O_7^{4-}]_{tot}$ = (4–80) × 10^{-3} M, and $[H^+]_{free} = 0.04$–0.40 M, with $I = 0.50$ M ($LiClO_4$). Two consecutive stages were observed, and rate constants for each were calculated using standard consecutive reaction treatment.[11] A very slow increase in the final absorbance was also observed, presumably due to slow formation of other products. The spectrophotometric changes for the latter were sufficiently small as not to interfere with the determination of the final absorbance.

The stopped-flow method was also used to investigate the complexing of HF to TiO^{2+}. Reactant concentrations were [Ti(IV)] = (0.9–3.6) × 10^{-3} M, [HF] = (0.89–7.2) × 10^{-2} M, and $[H^+]$ = 0.112–0.475 M, with $I = 0.50$ M ($LiClO_4$).

Other Reactants. Attempts to further extend the range of studies by including the complexing of Cl^-, Br^-, $CH_3CO_2^-$, $CCl_3CO_2^-$, and N_3^- with TiO^{2+} were not successful.

Treatment of Data. A nonlinear least-squares program with weighting $1/k^2$ was used unless otherwise stated.[12]

Results

Equilibration with NCS^-. Data obtained is consistent with a 1:1 equilibration

$$TiO^{2+} + NCS^- \underset{k_b}{\overset{k_f}{\rightleftharpoons}} TiO(NCS)^+ \tag{2}$$

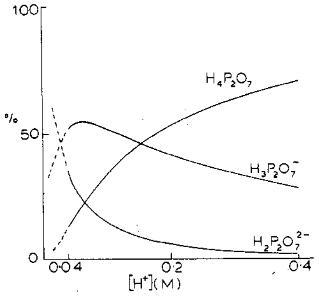

Figure 2. Species distribution of pyrophosphate ions over the $[H^+]$ range used in kinetic runs, as calculated from experimentally determined protonation constants at 25.0 °C, $I = 0.50$ M ($LiClO_4$).

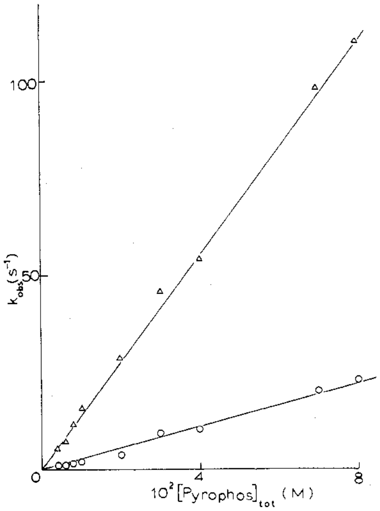

Figure 3. Plot of experimental first-order rate constant (25.0 °C) against $[P_2O_7^{2-}]_{tot}$ for the first (△) and the second (○) stages of the reaction of pyrophosphate with TiO^{2+}, $[H^+]_{free} = 0.10$ M, $I = 0.50$ M ($LiClO_4$).

Reciprocal relaxation times (τ^{-1}) are listed in Table II and give a good fit to eq 3, as illustrated in Figure 1. No dependence on $[H^+]$ was observed. At 25 °C, $I = 0.50$ M ($LiClO_4$), $k_f = (2.21 \pm 0.1) \times 10^3\ M^{-1}\ s^{-1}$ and $k_b = (7.2 \pm 0.1) \times 10^2\ s^{-1}$. Activation parameters are $\Delta H_f^\ddagger = 11.7 \pm 1.9$ kcal mol^{-1}, $\Delta S_f^\ddagger = -4 \pm 6$ cal K^{-1} mol^{-1}, $\Delta H_b^\ddagger = 14.9 \pm 1.0$ kcal mol^{-1}, and $\Delta S_b^\ddagger = 4.6 \pm 3$ cal K^{-1} mol^{-1}. Data at $I = 0.10$ M ($LiClO_4$) listed elsewhere[9] gives $k_f = (6.06 \pm 1.2) \times 10^3\ M^{-1}\ s^{-1}$ and $k_b = (1.98 \pm 0.05) \times 10^3\ s^{-1}$ at 25.1 °C. The latter give $K_T = 3.1\ M^{-1}$. The spectrophotometrically determined value was $3.3 \pm 0.8\ M^{-1}$.

$$\tau^{-1} = k_f[NCS^-] + k_b \tag{3}$$

Complexing with Pyrophosphate. Protonation constants for pyrophosphate are given in Table I. These give a product distribution as in Figure 2 for the $[H^+]$ range 0.04–0.40 M. Species $P_2O_7^{4-}$ and $HP_2O_7^{3-}$ are present as <10^{-4}% of the total pyrophosphate concentration and are unlikely to participate therefore. Relevant (rapid) protonation equilibria are as in

$$H_2P_2O_7^{2-} \underset{K_{3H}}{\overset{+H^+}{\rightleftharpoons}} H_3P_2O_7^- \underset{K_{4H}}{\overset{+H^+}{\rightleftharpoons}} H_4P_2O_7 \tag{4}$$

where $K_{3H} = 36.3\ M^{-1}$ and $K_{4H} = 6.28\ M^{-1}$. Rate constants for complexing with TiO^{2+} are then defined by eq 5–7. Since

$$TiO^{2+} + H_2P_2O_7^{2-} \xrightarrow{k_{2H}} \tag{5}$$

$$TiO^{2+} + H_3P_2O_7^- \xrightarrow{k_{3H}} \tag{6}$$

$$TiO^{2+} + H_4P_2O_7 \xrightarrow{k_{4H}} \tag{7}$$

Table III. First-Order Rate Constants (k_{obsd}) for the Reaction of TiO^{2+} with Pyrophosphate, λ 330 nm, at 25 °C, I = 0.50 M ($LiClO_4$)

$[H^+]_{free}$, M	$10^4 \cdot$ [Ti(IV)], M	10^3[pyrophos]$_{tot}$, M	k_{obsd},[a] s^{-1}	k'_{obsd},[b] s^{-1}
0.04	10.0	10.0	20.0	2.04
0.04	20.0	20.0	33.3	3.70
0.06	8.0	8.0	15.7	1.93
0.06	10.0	10.0	17.3	1.84
0.06	20.0	20.0	34.5	4.13
0.10	4.0	4.0	5.50	1.00
0.10	6.0	6.0	7.25	1.12
0.10	8.0	8.0	11.8	1.68
0.10	10.0	10.0	15.5	1.89
0.10	20.0	20.0	28.6	4.03
0.10	20.0	30.0	46.0	9.3
0.10	20.0	40.0	54.0	10.4
0.10	20.0	70.0	98.0	20.5
0.10	20.0	80.0	110.0	23.2
0.20	4.0	4.0	4.37	0.81
0.20	6.0	6.0	6.10	1.04
0.20	8.0	8.0	10.9	1.54
0.20	10.0	10.0	12.3	1.64
0.20	20.0	20.0	23.8	3.27
0.30	4.0	4.0	4.20	0.74
0.20	8.0	8.0	9.60	1.39
0.30	10.0	10.0	11.8	1.53
0.30	20.0	20.0		3.13
0.40	8.0	8.0	9.70	1.27
0.40	10.0	10.0	10.4	1.54
0.40	20.0	20.0	23.2	3.00

[a] First stage. [b] Second stage.

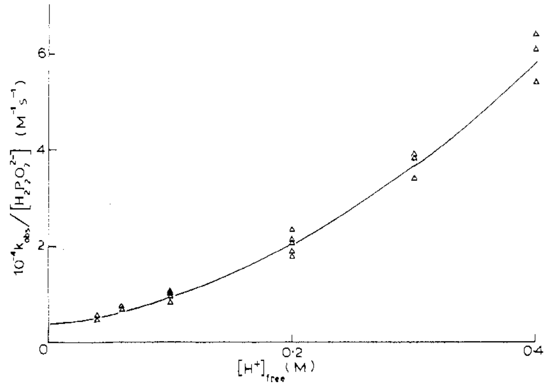

Figure 4. Plot of $k_{obsd}/[H_2P_2O_7^{2-}]$ against $[H^+]_{free}$ for the first stage of the reaction of pyrophosphate with TiO^{2+} at 25.0 °C, I = 0.50 M ($LiClO_4$).

$[P_2O_7^{4-}]$ and $[HP_2O_7^{3-}]$ are $\ll [H_2P_2O_7^{2-}]$, and the total pyrophosphate is in large excess over the titanium(IV) concentration, it follows that $[\text{pyrophos}]_{tot} = [H_2P_2O_7^{2-}] + [H_3P_2O_7^-] + [H_4P_2O_7]$, and the rate constant dependence (eq 8) can be derived. Values of k_{obsd} the experimentally observed

$$k_{obsd} = (k_{2H} + k_{3H}K_{3H}[H^+]_{free} + k_{4H}K_{3H}K_{4H}[H^+]^2_{free})[H_2P_2O_7^{2-}] \tag{8}$$

first-order rate constant are listed in Table III, and the linear dependence of k_{obsd} on $[\text{pyrophos}]_{tot}$ is illustrated in Figure 3. The best computer fit of experimental data to eq 8 is shown in Figure 4. Rate constants obtained from this fit are $k_{2H} = (3.6 \pm 0.6) \times 10^3$ M^{-1} s^{-1}, $k_{3H} = (0.95 \pm 0.3) \times 10^3$ M^{-1} s^{-1}, and $k_{4H} = (1.1 \pm 0.2) \times 10^3$ M^{-1} s^{-1}.

Observed rate constants for the second stage of reaction k'_{obsd} (linearity ≥80%) also exhibit a first-order dependence on pyrophosphate (Figure 3) and are accordingly assigned to formation of a 2:1 ligand to metal complex. A similar treatment of data in terms of a reaction sequence as in eq 5–7 and expression 8 gives $k'_{2H} = (0.52 \pm 0.61) \times 10^2$ M^{-1} s^{-1}, $k'_{3H} = (3.0 \pm 1.2) \times 10^2$ M^{-1} s^{-1}, and $k'_{4H} = (0.59 \pm 0.3) \times 10^2$ M^{-1} s^{-1}. No attempt was made to determine activation parameters.

Table IV. First-Order Rate Constants for the Reaction between TiO^{2+} and HF, I = 0.50 M ($LiClO_4$), λ 295 nm

Temp, °C	$[H^+]$, M	$10^3 \cdot$ [Ti(IV)], M	$10^2 \cdot$ [HF], M	k_{HF}, s^{-1}
25.0	0.25	0.92	0.89	18.4
	0.25	1.85	1.78	33.5
	0.25	0.92	1.78	34.4
	0.11	1.80	1.80	32.8
	0.19	1.80	1.80	33.6
	0.27	1.80	1.80	34.4
	0.29	1.80	1.80	34.0
	0.37	1.80	1.80	33.3
	0.48	1.80	1.80	34.8
	0.25	1.85	3.56	64.8
	0.25	3.70	3.56	65.5
	0.25	3.70	7.10	12.8
20.0	0.25	0.45	0.85	14.0
	0.25	0.90	0.85	15.0
	0.25	1.80	1.70	25.5
	0.25	3.60	3.40	47.0
	0.25	3.60	4.55	64.0
	0.25	3.60	5.70	81.5
	0.25	3.60	6.85	97.0
15.0	0.25	0.90	0.89	9.0
	0.25	1.80	1.75	17.3
	0.25	3.60	3.60	39.5
	0.25	3.60	4.80	50.0
	0.25	3.60	6.00	63.0
	0.25	3.60	7.20	72.0
6.0	0.25	0.90	0.85	6.0
	0.25	1.80	1.70	7.9
	0.25	3.60	3.40	16.5
	0.25	3.60	4.55	22.3
	0.25	3.60	5.70	32.0
	0.25	3.60	6.85	40.0

Complexing with HF. For the range of $[H^+]$ investigated <1% of the total fluoride is present as F^-. Concentrations of HF were ≥10-fold excess over that of TiO^{2+}. First-order rate constants k_{HF}, Table IV, gave no dependence on $[H^+]$ and exhibited a first-order dependence on [HF]. For an equilibration

$$TiO^{2+} + HF \underset{k_b}{\overset{k_f}{\rightleftharpoons}} TiO(F) + H^+ \tag{9}$$

an expression (eq 10) should apply, since fluoride ligands are

$$k_{HF} = k_f[HF] + k_b[H^+] \tag{10}$$

generally only weakly protonated for the range of $[H^+]$ under investigation.[13] However, the intercept in Figure 5 corresponding to k_b is only small, and we were unable to confirm the $[H^+]$ dependence in eq 10. At 25 °C, I = 0.50 M ($LiClO_4$), $k_f = 1.86 \times 10^3$ M^{-1} s^{-1}, $\Delta H_f^\ddagger = 10.6 \pm 1.0$ kcal mol^{-1}, and $\Delta S_f^\ddagger = -8.0 \pm 2.5$ cal K^{-1} mol^{-1}. From the magnitude of the intercept, $[H^+]$ = 0.25 M, the overall formation constant (k_f/k_b) is >200.

Discussion

No dependence on $[H^+]$ was observed in the 1:1 equilibration of TiO^{2+} with NCS^-, and participation of hydroxo Ti(IV) species in the kinetics is therefore ruled out. The kinetics at 25 °C, I = 0.10 M ($LiClO_4$), give a formation constant of 3.1 M^{-1} in good agreement with a value 3.3 M^{-1} from spectrophotometric studies. From activation parameters for the forward and reverse reaction, I = 0.50 M ($LiClO_4$), the thermodynamic parameters are $\Delta H = -3.2$ kcal mol^{-1} and $\Delta S = -8.6$ cal K^{-1} mol^{-1}, which are to be compared with values $\Delta H = -4.1$ kcal mol^{-1} and $\Delta S = -2.8 \pm 2.0$ cal K^{-1} mol^{-1} for the 1:1 complexing of NCS^- with VO^{2+}.[14]

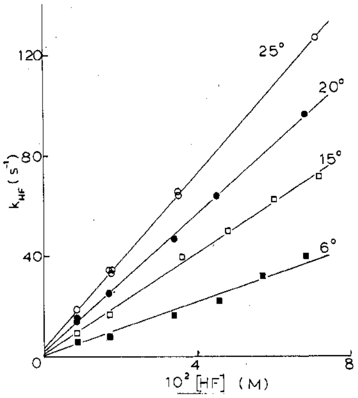

Figure 5. Plot of k_{HF} against [HF] for the reaction of TiO^{2+} with HF, I = 0.50 M ($LiClO_4$).

Table V. Kinetic Data for the 1:1 Complexing with TiO^{2+} at 25 °C

Reactant	I,[a] M	$10^{-3}k_f$, M^{-1} s^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal K^{-1} mol^{-1}
NCS^-	0.10	6.06		
NCS^-	0.50	2.21	11.7	−4.0
HF	0.50	1.86	10.6	−8.0
$H_4P_2O_7$	0.50	1.10 (k_{4H})		
$H_3P_2O_7^-$	0.50	0.95 (k_{3H})		
$H_2P_2O_7^{2-}$	0.50	3.60 (k_{2H})		

[a] I adjusted with $LiClO_4$.

A 1:1 reaction is also observed with hydrogen fluoride. The lack of a dependence on $[H^+]^{-1}$ is evidence against F^- participation. Small contributions only were obtained from the back-reaction (intercept in Figure 5), and precise evaluations of data for this step were not possible. Since protonation of coordinated fluoride is generally not extensive[13] an $[H^+]$ dependence (eq 10) is assumed for k_b, and this gives a limit to the formation constant of >200. Such a high value is consistent with a hard–hard ligand–metal interaction.

No back-reaction is observed in the anation of TiO^{2+} with pyrophosphate, and the most likely implication is that this ligand chelates. Complexing of pyrophosphate to VO^{2+} is also very favorable.[15] Two stages were detected in the kinetics and the dependence of both on the concentration of pyrophosphate clearly implicates formation of 1:1 and 2:1 ligand to metal complexes. A significant and very necessary part of this study was the determination of the protonation constants for pyrophosphate at 25 °C, I = 0.50 M ($LiClO_4$). Protonated species $H_4P_2O_7$, $H_3P_2O_7^-$, and $H_2P_2O_7^{2-}$ contribute to the rate law for the $[H^+]$ range investigated. Rate constants for the first stage indicate a clearcut enhancement for the 2− reactant, which can be explained in terms of electrostatic interactions to give a more favorable outer-sphere complexing constant K_{OS}. Rate constants for the second stage are not considered further because the charge on the 1:1 complex is not known.

Values of k_f, Table V, fall within a sufficiently narrow range as to suggest an I_d mechanism. At higher ionic strengths, such as 0.50 M used in this study, it becomes increasingly difficult to estimate realistic values of K_{OS} and hence calculate rate constants k for inner-sphere complexing as defined by the sequence

$$TiO^{2+} + L^{n-} \overset{K_{OS}}{\rightleftharpoons} TiO^{2+}, L^{n-} \tag{11}$$

$$TiO^{2+}, L^{n-} \xrightarrow{k} TiOL^{(2-n)+} \tag{12}$$

Since for NCS^- a strictly linear dependence of k_{obsd} on NCS^- is observed it can be concluded that K_{OS} < 0.3 M^{-1}. At I = 0.10 M calculated values of K_{OS} for a 2+ metal ion are in the range 0.3 M^{-1} (neutral ligand) to 13 M^{-1} (2− ligand).[16] Although these are not strictly applicable at I = 0.50 M, they do indicate an order of magnitude for k of 10^3 s^{-1}. The latter provides an estimate of k_{ex} for water exchange on TiO^{2+}, which has not as yet been determined.

Table VI. Kinetic Data for the 1:1 Complexing of VO^{2+} and Mo(V) Dimers at 25 °C

Metal ion	Reactant	I, M	$10^{-3}k_f$, M^{-1} s^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal K^{-1} mol^{-1}	Ref
VO^{2+}	NCS^-	0	11.5	10.8	−3.7	14
VO^{2+}	NCS^-	0.105	5.65			14
VO^{2+}	$^+NH_3CH_2$-CO_2^-	0.20	1.30	12.0	−4.0	15
VO^{2+}	SO_4^{2-}	0.025	37.0			*a*
VO^{2+}	$H_2P_2O_6^{2-}$	1.0	7.5[b]			15
VO^{2+}	$H_2P_2O_7^{2-}$	1.0	23[b]			15
VO^{2+}	H_2O	. . .	0.5[c]	13.3	−1.5	20
$Mo_2O_4^{2+}$	NCS^-	2.0	2.9	11.3	−0.3	21
Mo_2O_4-$(C_2O_4)_2^{2-}$	NCS^-	1.0	0.5	11.2	−4.2	18
Mo_2O_4-$(C_2O_4)_2^{2-}$	py	1.0	0.3	10.8	−6.5	18

[a] H. Strehlow and H. Wendt, *Inorg. Chem.*, **2**, 6 (1963). [b] At 12.0 °C. [c] Unit in s^{-1}.

An I_d assignment has also been suggested (at least tentatively) for the complexing of oxo ions VO^{2+} [17] and $Mo_2O_4^{2+}$.[18] The data for VO^{2+}, Table VI, is more difficult to assess because of the variety of ionic strength conditions used. Also, in the study of the complexing of VO^{2+} with pyrophosphate,[15] it has been assumed that only $H_2P_2O_7^{2-}$ is reactive at pH 2 and protonation constants determined in 1.0 M tetramethylammonium chloride solution at 25 °C have been used for a study in 1.0 M ($NaClO_4$) at 12 °C. In spite of a variety of interpretations[15] we feel that the prevailing pattern is in fact dissociative. Gordon and co-workers[19] have made the interesting suggestion that, in the coordination of glycine, $^+NH_3CH_2CO_2^-$ to VO^{2+}, reaction may proceed with initial occupancy of the very labile trans oxo position.[20] This will give a higher preequilibrium constant than if K_{OS} alone were effective. Subsequently rate determining loss of an equatorial H_2O ligand can occur to yield the equatorially substituted monodentate product. Whether such a mechanism has more general applicability remains to be seen. With Mo(V) substitution at least such a mechanism is unlikely to apply. Thus 1:1 complexing of the aquo dimer $Mo_2O_4^{2+}$ with NCS^- [21] and of the $Mo_2O_4(C_2O_4)_2(H_2O)_2^{2-}$ complex[18] (which has H_2O's cis to the terminal oxo ligands[22]) with NCS^- give very similar kinetic data. Second-order rate constants favor the aquo dimer by a factor of ca. 5, which can be accounted for by a statistical factor (×2) arising from the number of replaceable H_2O's, as well as the more favorable ion pairing of the (binuclear) 2+ reactant with NCS^-. Activation parameters for the reaction of TiO^{2+} with NCS^- and HF are in good agreement, and lend further support to an I_d assignment. The similarity of kinetic data for TiO^{2+} (d^0), VO^{2+} (d^1), and $Mo_2O_4^{2+}$, where Mo(V) (d^1) is in a dimeric situation with metal–metal bonding, is also very striking. With VO^{2+} and $Mo_2O_4^{2+}$ lengthening of the bond trans to the terminal oxo groups is well documented[23,24] and is likely to be effective also for TiO^{2+}. If such is the case then the process under investigation is presumably that giving substitution at an equatorial site of the TiO^{2+}. The present view is that coordination at the trans position as the only observable process would be expected to proceed much more rapidly.[20] In the case of $Mo_2O_4(C_2O_4)_2(H_2O)_2^{2-}$ the trans position is not available.[22]

The complexing of H_2O_2 with TiO^{2+} has been studied previously, I = 3.00 M ($NaClO_4$).[25] Rate constants give a good fit to the $[H^+]$ dependence $k_{obsd} = k_0 + k_1[H^+] +$

$k_2[H^+]^2$. Contributions from the $[H^+]$-dependent terms are small however (k_{obsd} is 125 M^{-1} s^{-1} at $[H^+] = 0.1$ M and 350 M^{-1} s^{-1} at $[H^+] = 3.0$ M). The rate constant $k_0 = 120$ M^{-1} s^{-1} at 25 °C is to be compared with values in Table V.

Registry No. TiO^{2+}, 12192-25-5; NCS^-, 1111-68-8; HF, 7664-39-3; $H_4P_2O_7$, 2466-09-3.

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The Relative Basicity of 4-Cyclohexylphosphorin and Aryl Phosphines from Hydrogen Bonding Studies

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The 1:1 equilibrium constants (K_1) have been determined in carbon disulfide by an infrared technique for the association of *p*-trifluromethylphenol with various para-substituted triphenylphosphines, 4-cyclohexylphosphorin, and 4-*tert*-butylpyridine. The relative Lewis basicities established from the equilibria studies on the phosphines are: tri-*p*-methoxyphenylphosphine ≫ 4-cyclohexylphosphorin > tri-*p*-methylphenylphosphine ≈ tri-*p*-chlorophenylphosphine > triphenylphosphine. 4-Cyclohexylphosphorin has a K_1 which is 36 times smaller than the similarly substituted nitrogen analogue, 4-*tert*-butylpyridine.

Introduction

It has long been recognized that phosphine, the phosphorus analogue of ammonia, and its alkyl and aryl derivatives represent an important class of bases with widely varying basicities. The pK_a of phosphine in aqueous solution has been estimated to be −14 from kinetic measurements[1] whereas the pK_a of diethylphenylphosphine is reported to be 6.25 in water.[2] An even larger value (9.7) is estimated for tricyclohexylphosphine.[3] In the gas phase the proton affinity of phosphine is less then that of ammonia, but trimethylphosphine has a larger proton affinity than trimethylamine.[4] This is contrasted with the conclusion of Henderson and Streuli[2] that in aqueous solution "a phosphine with a given number of alkyl substituents is a weaker base than an amine of the same $\Sigma\sigma^*$ value". In studies involving Lewis acids amines are more basic than phosphines in reactions with $AlMe_3$, $GaMe_3$, BMe_3, and BF_3 but the reverse is found for BH_3.[5] The large variation in basicity for aryl and alkyl phosphines has also been observed in the tendency of these ligands to form metal complexes with unusual stabilities and properties.[6] Recently, the kinetic reactivity of iridium phosphine complexes ($Ir(CO)ClL_2$, L = tertiary aryl phosphine) toward oxidative addition of methyl iodide was observed to change dramatically upon substitution at the para position of the phenyl ring.[7]

The phosphorus analogue of pyridine, phosphorin, has recently been synthesized[8] and the physical and chemical properties of this compound and its substituted derivatives are under investigation in several laboratories. The 2,4,6-triphenyl- and tri-*tert*-butyl-substituted phosphorins form stable π complexes when reacted with chromium hexacarbonyl.[9a] Nainan and Sears observed that 4-cyclohexylphosphorin forms stable complexes with other transition metals; in the reaction of 4-cyclohexylphosphorin[4] and chromium hexacarbonyl they find that this ligand exhibits bidentate character.[9b] Theoretical calculations employing[10] the CNDO/2 method indicate that phosphorin should have an aqueous pK_a of −10, but to date all attempts at producing the phosphorium cation have failed. This is, in part, due to the facile oxidation of phosphorin by $HClO_4$ and H_2SO_4. It has also been reported (unpublished data) that[11] "Addition of trifluoroacetic acid to cyclohexane solutions of various λ^3-phosphorins fail to produce any change in the UV spectra". Several efforts in our laboratories to measure the Gibbs free energy of formation of the 4-cyclohexylphosphorin cation have also failed to produce an unambiguous value for the quantity due to oxidation and side reactions. Consequently, it seems unlikely that a simple determination of the basicity of phosphorin will be forthcoming in the near future.

Hydrogen bonding studies have been shown to be a convenient means of determining the relative basicity of a related series of compounds.[12,13] For example, in the substituted pyridine series it has been shown that the hydrogen bonding basicities correlate with the aqueous pK_a values[14] and the gas phase proton affinities.[15] In view of the experimental diffi-