pyrazine (molten, 50 °C), react with the osmocenium dimer, yielding the metalated complex $[\{Cp(C_5H_4)Os\}_2]^{2+}$, osmocene, and noncrystalline intractable materials, while NH_3 and pyridine yield only intractable materials. As a result, these reactions have not been pursued further.

Reaction of $[Cp_2OsNCCH_3][PF_6]_2$ with X (X = Br^-, I^-, N_3^-). One other possible route toward new Os(IV) derivatives is to use existing Os(IV) complexes in substitution reactions. It is expected that these reactions would be less likely to follow alternate pathways that are apparently available to the more reactive $[(Cp_2Os)_2]^{2+}$. The substitution of Br^- and I^- for CH_3CN in $[Cp_2OsNCCH_3]^{2+}$ yielding $[Cp_2OsX]^+$ (X = Br, I) derivatives suggests that this approach has merit. The scope of this substitution reaction has not yet been fully explored.

On the other hand, reaction with N_3^- does not result in substitution. This appears to confirm the implication that N_3^- does not sufficiently stabilize Os(IV) and prefers to react by alternate pathways as was observed in the attempted disproportionation of $[(Cp_2Os)_2]^{2+}$ with azide. In this case, alternate redox pathways involving the metal are not readily available and instead the nucleophile attacks the Cp ring. The Cp ring in these higher valent Os metallocenes is activated toward nucleophilic attack. Such ring attack is precedented by the reaction of $[Cp_2RuBr]^+$ with water, where one cyclopentadienyl ring is converted to a cyclopentadienone ligand.[21]

Summary

The complex $[(Cp_2Os)_2]^{2+}$ is an important synthetic entry into the study of higher oxidation state Os metallocenes. The chemistry surveyed indicates that a variety of ligand-dependent reaction pathways are available to this complex or its derivatives. These include radical, disproportionation, and substitution routes. As a result, a number of previously unknown Os metallocene derivatives have been discovered and routes toward new complexes have been outlined. Additionally, the close analogy between $[(Cp_2Os)_2]^{2+}$ and $[Cp_2Re]_2$ suggests that similar chemistry may be developed for Re metallocenes.

Acknowledgment. Support of this work by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by the National Institutes of Health (Grant No. GM13638), is gratefully acknowledged. We also wish to acknowledge helpful discussions concerning X-ray crystallography with Drs. B. Hedman and A. L. Roe of Stanford University.

Registry No. $[(Cp_2Os)_2][PF_6]_2$, 107272-09-3; $[\{Cp(C_5H_4)Os\}_2][PF_6]_2$, 107272-11-7; Cp_2Os, 1273-81-0; $[NH_4]_2[Ce(NO_3)_6]$, 16774-21-3; $[Cp_2OsNCCH_3][PF_6]_2$, 107272-13-9; $[Cp_2OsSC(NH_2)_2][PF_6]_2$, 107272-15-1; $SC(NH_2)_2$, 62-56-6; $[C_{10}H_8Os]_n$, 107272-16-2; $(PNP)N_3$, 38011-36-8; $[Cp_2OsNO_3][PF_6]$, 107272-18-4.

Supplementary Material Available: Listings of anisotropic temperature factors and root-mean-square amplitudes of thermal vibration, complete listings of bond lengths and bond angles, and listings of calculated H atom positions and Cp ring plane calculations (12 pages); listings of observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

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The Titanyl Question Revisited

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Received September 24, 1986

The qualitative and quantitative composition of acidic aqueous solutions of dilute hydrolyzed Ti(IV) has been investigated by ^{17}O NMR spectroscopy supported by light-scattering experiments and UV, FTIR, and Raman spectroscopy. $[H^+]$- and $[Ti(IV)]_{total}$-dependent ^{17}O NMR experiments show unambiguously that oligomeric Ti(IV) species are formed at low $[H^+]$ and relatively high $[Ti(IV)]_{total}$ ($\gtrsim 0.05\ m$). The data are analyzed on the basis of a model system containing two trimers ($Ti_3O_4^{4+}$ (A) and $Ti_3O^{\alpha}{}_3O^{\beta}{}_2H_3^{5+}$ (B)) and a tetramer ($Ti_4O^{\alpha}{}_4O^{\beta}{}_2H_4^{8+}$ (C)) apart from monomeric species. The formation constants for the oligomer formations from TiO^{2+} in aqueous $HClO_4$ at 298 K and $\mu = 4.0\ m$ are $K_3^3 = 0.38 \pm 0.06$, $K_3^2 = 1.64 \pm 0.06\ m^{-1}$, and $K_4^1 = 2.31 \pm 0.03\ m^{-3}$, respectively. Possible implications for substitution and electron-transfer reactions of Ti(III) and Ti(IV) are discussed. Oxygen-exchange rates of the oxo, hydroxo, and aqua ligands of all the species involved have been determined qualitatively by the analysis of the temperature-dependent line widths of the ^{17}O NMR signals (oxo and hydroxo bridges, $k_{ex}{}^{298} \approx 100 \pm 50\ s^{-1}$; terminal H_2O or OH^- of oligomers, $k_{ex}{}^{298} \approx 3400 \pm 200\ s^{-1}$ (limit for slowest exchanging terminal H_2O or OH^- ligands); TiO^{2+} (rate measured in 68% aqueous methanol), $k_{ex}{}^{298} \approx 16\,000 \pm 5000\ s^{-1}$). This is a surprising result in terms of the yl oxygen since it is exchanging about 9 orders of magnitude faster than the yl oxygen in the thoroughly investigated VO^{2+} ion. This enormous difference is explained by a change of the exchange mechanism, and some theoretical and experimental indications for protonation of the yl oxygen of TiO^{2+} are presented.

Introduction

Yl-type metal oxo ions ($MO_n{}^{m+}$, n = 1, 2) are well-known for many metal centers, in particular for highly oxidized ions (e.g. V(IV),[2-4] Cr(V),[5] Mo(V) and -(VI),[6,7] W(V) and -(VI),[8] Os(VI),[9] Re(V),[10,11] U(VI),[12] etc.). However, simple monomeric and first-row transition-metal oxo ions seem not to be very common. The probably best known and thoroughly studied vanadyl ion[2-4] is quite special in both respects. It is then an obvious question whether Ti(IV), the highly oxidized neighbor of V(IV), does form

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titanyl species of some sort. In spite of the increasing interest in the aqueous chemistry of Ti(IV) (e.g. the importance of TiO_2 colloids as supports for catalysts, as for photochemical water-splitting systems[13]), although various studies on electron transfer and substitution involving the putative titanyl ion (TiO^{2+}) have been reported,[14-29] only very sparse thorough information about the aqueous chemistry of Ti(IV) is known. Textbooks still describe the titanyl unit as "nonexistent" or at least "unproven",[30] and it seems to be generally accepted that Ti(IV) complexes with a true titanyl core are quite rare.[31,32] Indeed, until recently crystallographic and spectroscopic evidence for a TiO^{2+} moiety was only available for a few examples (TiO(porphyrin),[33] TiO(phthalocyanine),[34] $TiOCl_4^{2-}$,[35] $TiOF_5^{3-}$[36]). The only evidence for monomeric titanyl in dilute solutions of Ti(IV) in aqueous acid was from indirect techniques such as ion exchange,[37,39] potentiometric titration,[38] electromigration,[39] and kinetic studies of electron-transfer and complexation reactions.[14-29] Alternatively, the species present in solution were claimed to be true titanyl (TiO^{2+}(aq)) or the related dihydroxo species ($Ti(OH)_2^{2+}$(aq)). From this earlier work it was concluded that in dilute acidic solutions only monomeric species with a 2+ charge are present.[14,15,37-39] Recently, direct evidence for TiO^{2+}(aq) from Raman spectroscopy[40] and EXAFS measurements[41] was produced. The important question, however, of whether TiO^{2+}(aq) is the only species in solution, viz. to what extent it is in equilibrium with the dihydroxo species ($Ti(OH)_2^{2+}$(aq)), with protonated monomers, and with oligomeric species has not been directly addressed before. In this contribution we report on further spectroscopic and semiquantitative kinetic results on hydrolyzed Ti(IV) ions in dilute acidic solutions.

Experimental Section

Preparation of the Solutions. A purified and analyzed sample of $TiOSO_4 \cdot 2H_2O$ (Anal. Calcd: Ti, 24.44. Found: Ti, 24.48) was donated by F. P. Rotzinger.[40] All solutions were prepared as follows: The required amount of aqueous acid with known [H^+] at 15.0 °C was added to a known amount of $TiOSO_4 \cdot 2H_2O$ and, where required, $Mn(ClO_4)_2 \cdot 3H_2O$ or $Gd(ClO_4)_3 \cdot 5.7H_2O$. The solution was stirred at 15.0 °C in a closed vessel until complete dissolution took place (~24 h). A solution of $Ba(ClO_4)_2 \cdot 6H_2O$ in a small amount of H_2O with a known amount of Ba^{2+} was added dropwise and the mixture stirred for ca. 6 h at 15.0 °C. Then, $BaSO_4$ was removed by centrifugation below 15 °C. In some cases either $Mn(ClO_4)_2 \cdot 3H_2O$ or $Gd(ClO_4) \cdot 5.7H_2O$ was added subsequently. Where methanol was used, it was usually added as the solvent of the Ba^{2+} salt. The ionic strength was adjusted with $NaClO_4$, $Ba(ClO_4)_2$ (excess), or $Al(ClO_4)_3$, except for vibrational spectroscopy, where the chloride salts were used. The labeled water of known purity was introduced in the aqueous acid and the Ba^{2+} solutions and the amount of ^{17}O label corrected for ~~the various~~ hydrates ~~added.~~ For one experiment $TiCl_4$ was directly hydrolyzed in aqueous acid with a known amount of ^{17}O label. Where necessary the solutions were Millipore filtered (MF-Millipore filters, 0.3-μm pore size). All solutions were kept in the refrigerator. It was shown that the solutions are stable to formation of colloidal TiO_2 for at least 4 weeks when refrigerated, particularly for solutions with low [Ti(IV)] and high [H^+]. However, all measurements reported herein are from fresh solutions (typically less than 2 days). Ion-exchange experiments were performed with Dowex 50W-X2 resins. The amount of recovered Ti(IV) was determined spectrophotometrically as described in the literature.[14] Enriched (^{17}O)water was from Yeda R+D, Rehovot, Israel. Natural water was doubly distilled, and all other chemicals were of purissimum p.A. or similar degrees.

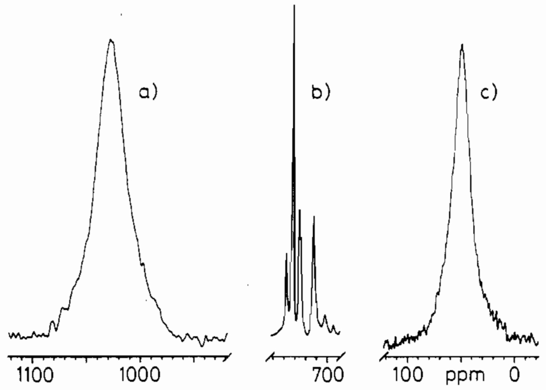
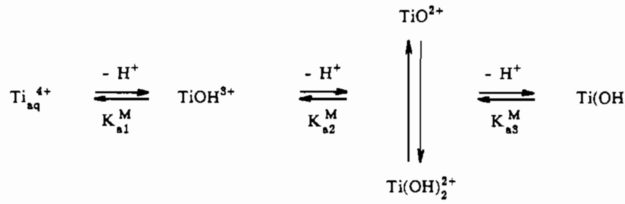


Figure 1. Typical ^{17}O NMR spectra of hydrolyzed Ti(IV) (numbering of solutions refers to Table I): (a) solution 25, monomeric TiO^{2+}; (b) solution 9, oxo and hydroxo bridges of oligomeric species; (c) solution 1, terminal water and hydroxide of oligomeric species.

Scheme I



Physical Measurements. **^{17}O NMR spectra** were recorded at 54.245 MHz on a Bruker AM 400 instrument equipped with a wide-bore cryomagnet and an Aspect 3000 data system. The sweep width was 50 000 Hz (100 000 Hz for the spectra of terminal H_2O and of the titanyl signal), the pulse length (PW) was 14.0 μs, the acquisition time (AQ) was 0.020 48 s, and the number of pulses employed was 1.2×10^6 (100 000 for spectra of the titanyl signal); for the relatively broad lines of the titanyl signal an exponential line broadening of 100 Hz was applied. Fast-injection experiments were performed with equipment described elsewhere.[42] All experiments were performed on nonspinning samples. The bulk water signal was usually suppressed by addition of a fast-exchanging paramagnetic relaxation agent. The paramagnetic relaxation agent used was either Mn(II) (high-temperature studies; 0.2 *m* $Mn(ClO_4)_2$; estimated line width of bulk water at 292 K $\Delta\nu_{1/2} \approx 3.3 \times 10^5$ Hz[43]) or Gd(III) (low-temperature studies; 0.1 *m* $Gd(ClO_4)_3$; estimated line width of bulk water at 212 K $\Delta\nu_{1/2} \approx 1.6 \times 10^6$ Hz[44]). It

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Table I. Concentration Dependences of the ^{17}O NMR Chemical Shifts (δ, ppm) and of the Oxygen Concentrations ([O], 10^{-3} *m*) Obtained from ^{17}O NMR Spectra[d]

	[Ti],	[H$^+$],	[ClO$_4^-$],	μ,	*T*,	signal 1		signal 2		signal 3		signal 4	signal 5	signals 4 + 5[a]	signal 6		signal 7	
soln	*m*	*m*	*m*	*m*	K	δ	[O]	δ	[O]	δ	[O]	δ	δ	[O]	δ	[O]	δ	[O]
1	*0.496*	2.02	3.35	4.02	293.1					731.1	85[b]	726.8	725.7	143	713.5	54	44.7	70
2	*0.397*	2.03	3.35	4.01	293.1					731.9	62[b]	727.1	726.0	80	712.9	39	45.1	39
3	*0.302*	2.01	3.35	4.01	292.8					732.1	48[b]	726.7	725.5	30	713.4	17		
4	*0.297*	2.03	3.35	4.01	293.1					731.2	47[b]	726.8	725.7	37	713.1	23	44.7	24
5	*0.253*	2.04	3.38	4.02	292.8					732.1	30[b]	726.6	725.4	18	713.5	11		
6	*0.201*	2.02	3.36	4.05	292.8					732.0	15[b]	726.7	725.5	8.5	713.5	6.7		
7	*0.198*	2.03	3.35	4.01	293.1					731.5	17[b]	726.7	725.5	9.7	713.3	7.4	44.8	6.7
8	*0.149*	2.00	3.34	4.03	292.8					732.0	6.1[b]	726.7	725.4	2.7	713.6	2.2		
9	*0.345*	0.98	2.97	3.96	292.8			737.2	22	731.9	65	725.6	724.3	35	712.4	37	44.3	44
10	*0.297*	0.96	2.94	3.93	292.8			737.8	17	732.0	54	725.6	724.2	26	712.4	31	44.3	25
11	*0.248*	0.98	2.98	3.98	292.8			738.0	13	732.0	41	725.6	724.1	20	712.3	24	45.2	
12	*0.201*	0.95	2.95	3.96	292.8			739.1	6.7	732.1	24	725.5	723.9	8.7	712.3	13		
13	*0.153*	0.99	2.99	3.98	292.8			738.6	3.6	732.0	12	725.6	724.1	4.3	712.5	6.3	45.2	7.0
14	0.201	*0.95*	2.95	3.96	292.8			739.1	6.7	732.7	24	725.5	723.9	8.7	712.3	13		
15	0.200	*1.51*	3.17	4.00	292.8			735.1	2.8	732.2	14	726.1	724.5	8.6	713.0	9.0		
16	0.201	*2.02*	3.36	4.03	292.8					732.0	15[b]	726.2	725.0	8.6	713.0	6.7		
17	0.200	*2.51*	3.53	4.04	292.8					731.1	9	726.0	724.8	9.1[b]	713.1	4.8		
18	0.208	1.04	*1.88*	*2.30*	292.8			740.9	4.3	732.0	14	725.2	723.3	2.8	712.0	4.3		
19	0.201	1.01	*3.62*	4.02	292.8			738.5	8.6	731.9	25	725.4	723.8	9.4	712.2	13		
20	0.201	1.01	*3.02*	4.03	292.8			738.6	5.8	732.0	22	725.5	723.9	9.1	712.3	12		
21	0.199	1.00	*2.72*	4.04	292.8			738.5	7.3	732.0	23	725.6	724.0	8.6	712.4	12		
22[c]	*0.050*	0.98	2.21	2.98	195.9	1027	6.2											
23[c]	*0.040*	0.99	2.23	3.00	195.9	1028	5.9											
24[c]	*0.030*	1.00	2.25	3.02	195.9	1027	4.2											
25[c]	0.030	*1.00*	2.25	3.02	195.9	1027	4.2											
26[c]	0.030	*1.48*	2.39	3.00	195.9	1028	2.2											
27[c]	0.030	*1.96*	2.54	2.98	195.9	1030	1.2											

[a] Signals 4 and 5 are not fully resolved; their intensity ratios remain constant in all experiments. [b] Depending on [H$^+$], signal 2 is partly obscured by either signal 3 or signals 4 + 5; in these cases the integrated sum of signal 2 and the signals concerned is given. [c] H_2O/MeOH mixtures (68.2% MeOH). [d] For error limits, see ref 50.

has been checked that the addition of Mn(II) and Gd(III) has no influence on the qualitative and quantitative composition of the Ti(IV) solutions and on the ^{17}O line broadening. Chemical shifts are all vs. bulk water; where necessary ClO_4^- (δ = 289 ppm) was taken as internal standard. Positive chemical shifts are downfield. For intensity measurements the signal from ClO_4^- ($t_{1/2}$(oxygen exchange) $\gtrsim$ 100 years,[45] natural abundance of ^{17}O 0.037%) was used as the internal standard.

FTIR spectra were recorded on a Bruker IFS 113V instrument equipped with an Aspect 1000 system. AgCl windows with 50-μm sample layers were used.

Raman spectra were measured on a SPEX Ramalog spectrophotometer using an argon laser (λ = 514.5 nm, 0.8 W).

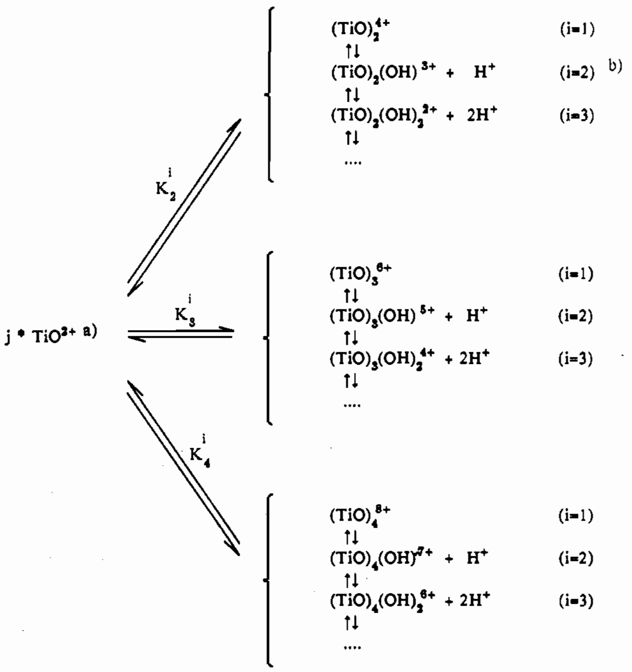
UV spectra were recorded on a Perkin-Elmer Hitachi or a Perkin-Elmer Lambda 7 instrument equipped with a Perkin-Elmer 3600 data station.

Light-scattering experiments were performed by using photon correlation on a Brookhaven Instruments correlator. Detection was by photon counting. The photomultiplier was mounted on a goniometer arm. The solutions were pumped through a closed system including the cell and a Millipore filter (MF-Millipore filters; 0.3-μm pore size) before each measurement. The light source used was a He/Ne laser (5 mW, λ = 632.8 nm).

Results

Analysis of Oligomers by ^{17}O NMR Spectroscopy and by Light Scattering. ^{17}O NMR signals of dilute hydrolyzed Ti(IV) in aqueous acid occur in three different chemical shift regions, i.e. around 1000–1100, 700–800, and 0–100 ppm (Figure 1, Table I). On the basis of the ^{17}O chemical shifts of comparable oxo species (e.g. Mo(V),[46] Mo(IV),[46] V(V),[47,48] etc.), yl-type oxygens, μ_2 bridging oxygens or hydroxides, and water or hydroxide, coordinated to monomeric or oligomeric Ti(IV) species, are respectively expected to occur in the above regions. At temperatures $\gtrsim$260 K only the last two sets of signals at 700–800 and 0–100

Scheme II



[a] The formation of the dihydroxo cation might also be involved: $TiO^{2+} + H_2O \rightleftarrows Ti(OH)_2^{2+}$. [b] $(TiO)_a(OH)_b^{c+}$ indicates a deprotonated oligomer. This does not necessarily imply coordination of OH^-.

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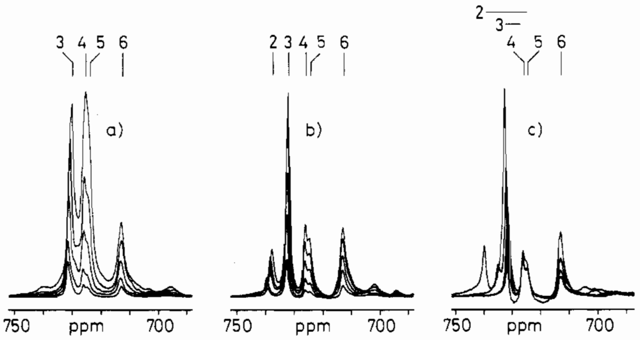

Figure 2. Concentration dependences of ^{17}O NMR signals for oxo and hydroxo bridges of oligomers in hydrolyzed Ti(IV) (numbering of solutions refers to Table I): (a) from top to bottom, solutions 1, 2, 4, 7, 8; (b) from top to bottom, solutions 9–13; (c) from top to bottom, solutions 14–17. For clarity not all spectra used for the calculations are plotted in the figure.

ppm were observable. They are attributed to oligomeric species (see below) and are only present in relatively concentrated solutions ($[\mathrm{Ti(IV)}] \gtrsim 0.05$ *m*; $1.0\ m < [\mathrm{H^+}] < 2.5\ m$). In preliminary ^{47,49}Ti NMR measurements at 11.200 MHz no signals were observed.[49]

In a first approximation the system of hydrolyzed Ti(IV) may be described as consisting of $\mathrm{TiO^{2+}(aq)}$ and its protonated and deprotonated derivatives and related oligomers (Schemes I and II). From the expressions for the equilibrium constants (eq 1–5)

$$K_{a1}{}^{M} = \frac{[\mathrm{TiOH^{3+}}][\mathrm{H^+}]}{[\mathrm{Ti^{4+}(aq)}]} \tag{1}$$

$$K_{a2}{}^{M} = \frac{[\mathrm{TiO^{2+}}][\mathrm{H^+}]}{[\mathrm{TiOH^{3+}}]} \tag{2}$$

$$K_{a3}{}^{M} = \frac{[\mathrm{Ti(OH)_3{}^+}][\mathrm{H^+}]}{[\mathrm{TiO^{2+}}]} \tag{3}$$

$$K_2^1 = \frac{[\mathrm{(TiO)_2{}^{4+}}]}{[\mathrm{TiO^{2+}}]^2} \tag{4}$$

$$K_2^2 = \frac{[\mathrm{(TiO)_2(OH)^{3+}}][\mathrm{H^+}]}{[\mathrm{TiO^{2+}}]^2}$$

$$\vdots$$

$$K_3^1 = \frac{[\mathrm{(TiO)_3{}^{6+}}]}{[\mathrm{TiO^{2+}}]^3} \tag{5}$$

$$K_3^2 = \frac{[\mathrm{(TiO)_3(OH)^{5+}}][\mathrm{H^+}]}{[\mathrm{TiO^{2+}}]^3}$$

$$\vdots$$

Table II. [Ti(IV)]-Dependent Light-Scattering Data of Hydrolyzed Ti(IV)

soln	[Ti], *m*	$[\mathrm{H^+}]$, *m*	$[\mathrm{ClO_4{}^-}]$, *m*	μ, *m*	*T*, *K*	$10^{-3}\times$ counts[a]	[oligomers],[b] *m*
1	0.67	1.99	3.32	3.99	293.1	166	0.0877
2	0.50	1.99	3.32	3.99	293.1	101	0.0534
3	0.40	2.00	3.33	3.99	293.1	44	0.0233
4	0.30	2.00	3.33	4.00	293.1	23	0.0122
5	0.20	2.00	3.33	3.99	293.1	17	0.00899
6	0.00	2.00	3.33	4.00	293.1	0	0.0

[a] Background corrected with solution 6. [b] Sum of the oligomer concentrations (counts = $f\sum_i\sum_j[\mathrm{OL}_i^j]$) (see Table III).

it is clear that equilibria between monomers are independent of $[\mathrm{Ti(IV)}]_{\mathrm{total}}$ whereas the formation of oligomers from monomers is dependent on $[\mathrm{Ti(IV)}]_{\mathrm{total}}$ and in most cases also on pH. An analysis of the $[\mathrm{Ti(IV)}]_{\mathrm{total}}$ and $[\mathrm{H^+}]$ dependencies on the oxygen concentrations per signal obtained from ^{17}O NMR spectroscopy should therefore yield some information on the various species involved. The results of the studies with variable $[\mathrm{Ti(IV)}]_{\mathrm{total}}$ and variable $[\mathrm{H^+}]$ are presented in Figure 2 and Table I (Table I also contains some measurements with variable perchlorate concentration and with variable ionic strength). $[\mathrm{Ti(IV)}]_{\mathrm{total}}$ has been checked spectrophotometrically,[14] and the absence of colloidal $\mathrm{TiO_2}$ (<2%) was shown by light-scattering measurements (both tests have been performed for some extreme cases with high $[\mathrm{Ti(IV)}]_{\mathrm{total}}$ and small $[\mathrm{H^+}]$ and for aged solutions only). At this point we have to stress that the intensities of the ^{17}O NMR signals in this study are subject to relatively large errors.[50] An examination of Figure 2a,b shows clearly that the dependence of the intensities of the various signals on $[\mathrm{Ti(IV)}]_{\mathrm{total}}$ is nonlinear. The species involved are therefore unambiguously oligomers. Apart from some minor additional signals, which are not accounted for in this analysis, there are five signals in this region and therefore not more than five different oligomers in solution under the present conditions (excluding overlapping signals). However, some intensity ratios remain constant and the system may therefore be described by less oligomers. The formation of oligomers is also clearly shown by the nonlinearity of the light-scattering measurements as a function of $[\mathrm{Ti(IV)}]_{\mathrm{total}}$ (Table II). Two points emerge from an examination of Figure 2c. First, the concentration of the oligomers is, with the exception of the oligomers responsible for signals 4 and 5, dependent on $[\mathrm{H^+}]$ (the increased intensity of signals 4 and 5 in spectrum 17 (see Table I) is explained with a shift of the lowest field signal (2) under the signals in question; see below). Second, the chemical shifts of signals 2 and 3 are dependent on $[\mathrm{H^+}]$. This high-field shift upon increasing $[\mathrm{H^+}]$ is attributed to a protonation of the oxo bridges concerned, and the knowledge of the relative basicities together with the relative chemical shifts of the oxo bridges leads to some qualitative structural information.

The analysis of the ^{17}O NMR intensities and of the amount of scattered light as a function of $[\mathrm{Ti(IV)}]_{\mathrm{total}}$ and $[\mathrm{H^+}]$ is related to the stoichiometries of the oligomers involved and to the relative formation constants. The analysis is based on the equilibria given in Scheme II. The numeric analysis involves a simultaneous nonlinear regression of all the data (Tables I and II), which is based on the general expression for oligomer formation shown by eq 6, where $[\mathrm{OL}_j^i]$ is the calculated concentration of any given

$$[\mathrm{OL}_j^i] = K_j^i/[\mathrm{H^+}]^{i-1}[\mathrm{TiO^{2+}}]^j \tag{6}$$

oligomer. The concentration of $\mathrm{TiO^{2+}}$ is not directly available. Therefore, it has to be calculated from $[\mathrm{H^+}]$, $[\mathrm{Ti(IV)}]_{\mathrm{total}}$, and initially estimated equilibrium constants K_j^i (eq 7). The root

$$\Big(\sum_j\sum_i j(K_j^i/[\mathrm{H^+}]^{i-1})[\mathrm{TiO^{2+}}]^j\Big) + [\mathrm{TiO^{2+}}] - [\mathrm{Ti(IV)}]_{\mathrm{total}} = 0 \tag{7}$$

$[\mathrm{TiO^{2+}}]$ of this polynomial is found iteratively by the method of Newton. The calculated $[\mathrm{TiO^{2+}}]$ and the experimental $[\mathrm{H^+}]$ are then used to obtain refined K_j^i values through eq 6. The procedure involving eq 6 and 7 is iterative.[51] The primary problem of such an analysis (apart from the experimental accuracy[50]) is the large number of model-dependent constants and fitted parameters. Clearly, it is justified to assume that in the spectral window of 700–800 ppm only oxo and hydroxo bridges are observed (see above) and that all bridging oxygens of oligomeric species are detectable in this spectral region (viz. their exchange rates are

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(49) This is presumably due to large line widths due to quadrupolar effects of the Ti nuclei and substantial acoustic ringing at the frequency employed. No effort has been made yet to suppress the latter effect.

(50) The oxygen concentrations per signal are calculated from the integrals as follows: $[\mathrm{O}] = (I(\mathrm{O})/I(\mathrm{ClO_4{}^-}))(4[\mathrm{ClO_4{}^-}](3.7\times10^{-4}))/(^{17}\mathrm{O}$ mole fraction $(\mathrm{H_2O}))$. The error limits for $[\mathrm{Ti(IV)}]_{\mathrm{total}}$, $[\mathrm{H^+}]$, $[\mathrm{ClO_4{}^-}]$, μ, and *T* (see Table I) are ±0.01 *m*, ±0.01 *m*, ±0.01 *m*, ±0.01 *m*, and ±0.2 K, respectively, the error in chemical shifts is ±0.5 ppm, and the approximate error of the calculated oxygen concentrations is ±20% (based on an integration error of ±10%).

(51) In cases where two or more ^{17}O NMR signals are overlapping and could not be resolved, the integrated sum is fitted to a mathematical expression similar to eq 6 describing the sum of two or more oligomeric species.

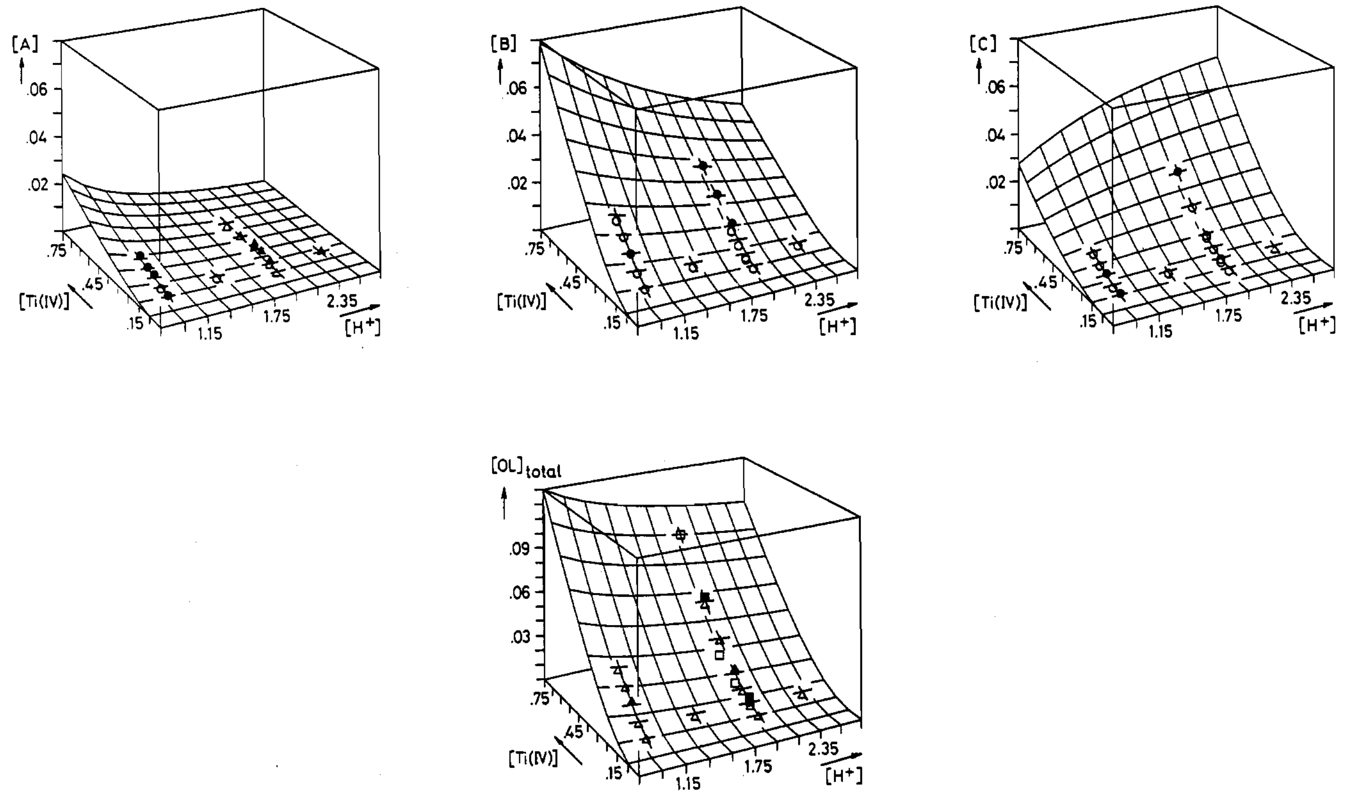

Figure 3. Oligomer concentrations (m) based on intensities of ^{17}O NMR signals of oxo and hydroxo bridges and of scattered light as a function of $[H^+]$ and $[Ti(IV)]_{total}$ fitted to eq 6 and 7: (circles) ^{17}O NMR data; (triangles) overlapping signals, calculated from the sum of integrals (see Table I); (boxes) light-scattering data. Solid symbols are above and open ones below the calculated surfaces (parameters for the calculation given in Table III).

similar (see below)). On the basis of the experimental ^{17}O NMR intensities, light-scattering data, and the data treatment described above, five parameters need to be fitted (viz. four equilibrium constants K_j^i (signals 4 and 5 could not be resolved in any instance and are therefore fitted together[51]) and one parameter adjusting the light scattering data to real concentrations). All other parameters (i.e. the nuclearity j, the number of protons released ($i - 1$), the number of bridging oxygens per signal and structural unit s, and correlation factors allowing several signals to belong to the same oligomeric species) are model-dependent. The data have been fitted for a large number of chemically reasonable model systems. It is found that the solutions are best described as containing the two different trimers A and B and the tetramer C apart from monomeric species. Trimer A has one type of μ-oxo

$$\underset{A}{Ti_3O_4{}^{4+}} \qquad \underset{B}{Ti_3O^{\alpha}{}_3O^{\beta}{}_2H_3{}^{5+}} \qquad \underset{C}{Ti_4O^{\alpha}{}_4O^{\beta}{}_2H_4{}^{8+}}$$

bridge; $i - 1 = 2$, viz. two protons are liberated upon formation, and this accounts for ^{17}O NMR signal 2 (most basic species). Trimer B has two types of μ-oxo and -hydroxo bridges; $i - 1 = 1$, viz. one proton is liberated upon formation, and this accounts for ^{17}O NMR signals 3 and 6 (relatively basic species). Tetramer C has two nonequivalent sets of μ-oxo and -hydroxo bridges; $i - 1 = 0$, and this accounts for ^{17}O NMR signals 4 and 5. The results of the fits are shown in Figure 3 and Table III. Details of the fitting procedures and detailed results (including details of the evaluation of "the best fit") are deposited as supplementary material.[52] We have to point out that the quality of the fit does not really prove the model retained, i.e. the presence of only three oligomers with stoichiometries A, B, and C. However, the model is supported by the fact that it is self-consistent in terms of the various types of experiments, viz. ^{17}O NMR intensities, chemical shifts, and scattered light vs. $[H^+]$ and $[Ti(IV)]_{total}$. Especially comforting is the fact that the equilibrium constant K_2^3 obtained independently from signals 3 and 6 is constant within the error (Table III).

Table III. Parameters for the System of Oligomers in Aqueous Acidic Solutions of Ti(IV) (Scheme II, Eq 6, Species A–C)

species	j^a	s^b	$i - 1^c$	$K_j^{i\,d}$	f^e
A	3	4	2	$K_3^3 = 0.38 \pm 0.06$	1892 ± 31
B^{α}	3	3	1	$K_3^2 = 1.66 \pm 0.04\ m^{-1}$	
B^{β}	3	2	1	$K_3^2 = 1.61 \pm 0.07\ m^{-1}$	
$C^{\alpha,\beta}$	4	6	0	$K_4^1 = 2.31 \pm 0.03\ m^{-3}$	

[a] Nuclearity of oligomers. [b] Number of oxygens involved. [c] Number of H^+ ions released upon formation of the oligomeric species. [d] Oligomer formation constant (298 K, $\mu = 4.0\ m$). [e] Factor adjusting the light-scattering counts to oligomer concentrations: counts = $f\sum_i\sum_j[OL_i^j]$.

The question of ion pairing and the dependence of the formation of oligomers on the ionic strength are addressed qualitatively with spectra 18–21 (Table I). At a constant ionic strength ($\mu = 4.0\ m$) and constant $[H^+]$ and $[Ti(IV)]_{total}$, perchlorate, which then governs the ion pairing, has been varied by varying the supporting electrolyte (solutions 21–19: $Al(ClO_4)_3$, $Ba(ClO_4)_2$, $NaClO_4$). In the limited $[ClO_4^-]$ range available in this way it appears from the experimental results that ion pairing of the various Ti(IV) species involved with ClO_4^- is negligible. As expected, there is a dependence of the concentration of oligomers on the ionic strength, however. With decreasing ionic strength the formation of oligomers is disfavored.

Analysis of Monomeric Species by Low-Temperature ^{17}O NMR, Raman, and FTIR Spectroscopy. In aqueous acidic solutions ($[Ti(IV)]_{total} = 0.5$–$0.05\ m$; $[H^+] = 1.0$–$2.5\ m$; $\mu = 4.0\ m$) there are no ^{17}O NMR signals for monomeric species in the temperature range 263–323 K. However, the oligomers (see Figure 3) account only for ca. 7–45% (solutions 8 and 1, respectively) of the total amount of Ti(IV) present, on the basis of the model used above. Furthermore, monomeric TiO^{2+} has been established in similar solutions by Raman and FTIR spectroscopy (see ref 40 and below) and by EXAFS measurements.[41] It is therefore obvious to assume

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(52) Details of the oligomer fits, calculations on the potentiometric titrations,[28] and pK_a determinations are given as supplementary material.

Table IV. Temperature Dependence of the Relaxation Rates $1/T_2{}^b$ of Coordinated Oxo Ligands of Hydrolyzed Ti(IV)[a]

soln	[Ti], *m*	[H$^+$], *m*	*T*, K	$1/T_2{}^b$, s^{-1} signal 1	signal 2	signal 3	signals 4 + 5[b]	signal 6	signal 7
9	0.345	0.984	293.5						2920
			304.7						3990
			307.9						5970
12	0.201	0.947	273.2			470	660	690	
			283.1		310	280	570	500	
			292.8		270	220	530	380	
			304.3		250	220	530	350	
28[c]	0.033	0.952	179.9	4240					
			199.1	5940					
			225.8	7790					
			242.9	11500					

[a] $1/T_2{}^b = (\Delta\nu_{1/2})\pi$. [b] The line width is for the sum of both signals. [c] 68% methanol.

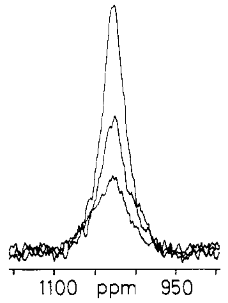

Figure 4. [H$^+$] dependence of the ^{17}O NMR signal of TiO^{2+}: from top to bottom, solutions 25, 26, and 27 (numbering refers to Table I; identical experimental conditions for all spectra).

that one fails to detect the ^{17}O NMR signals at 263 K already due to exchange broadening. The temperature therefore had to be decreased drastically, and that is only possible if one changes the solvent. This might have some undesired side effects. Indeed, there are some changes in the ^{17}O NMR spectra in the region of the oxo and hydroxo bridges of the oligomers, when some methanol is added. However, our goal was to detect and investigate monomeric TiO^{2+}. In any case TiO^{2+} will be solvated preferentially by the water present and some coordination of methanol will not have a primary effect on the reactivity of this species. This was shown clearly in experiments where methanol concentration was varied and where methanol was substituted by acetone.

At 195.85 K spectra of monomeric titanyl could be observed at 1028 ppm (Figure 1, Table I), a chemical shift region where yl-type oxygens are expected to occur. There is a linear dependence of the integral of the signal on $[\mathrm{Ti(IV)}]_{\mathrm{total}}$, and this indicates that the species is monomeric, indeed (Table I, spectra 22–24). In addition, there is a dependence of the observed amount of titanyl on [H$^+$]; i.e., the signal is disappearing with decreasing pH (Table I, spectra 25–27; Figure 4). The quantitative analysis of the spectra reveals that the amounts present as TiO^{2+} are 14, 7.5, and 4% for the solutions with [H$^+$] of 0.99, 1.48, and 1.96 *m*, respectively. This clearly indicates that TiO^{2+} is undergoing protonation equilibria under the conditions of our experiments. An estimate of the pK_a values on the basis of the ^{17}O NMR experiments is not warranted since the activity of H$^+$ in 68% methanol, the effect of some coordination of methanol to titanyl, nor the effect of the temperature on the pK_a values are known.

The symmetric A_1 mode of yl-type metal oxocations $\bar{\nu}_s$(M=O) is expected in the region 900–1000 cm^{-1}.[35,36,40] A polarized band at 975 cm^{-1} was found in aqueous acidic solutions of Ti(IV) and attributed to $\bar{\nu}_s$(Ti=O).[40] Since ClO$_4{}^-$ exhibits a very strong A_1 mode in the same region,[53,54] Raman and FTIR spectra were usually recorded in perchlorate-free media (dilute HCl; coordination of chloride can be neglected[16,40]). In IR spectroscopy we have observed a weak absorption at 974 cm^{-1}. Monomeric hydroxo and aqua species are expected to give rise to vibrations in the regions of 500 and 400 cm^{-1}, respectively.[55,56] No such signals could be resolved.[57] Also, no changes of frequency or line width of $\bar{\nu}_s$(Ti=O) as a function of pH could be observed.

Table V. Estimated Oxygen Exchange Rates $k_{\mathrm{ex}}{}^{298}$ (s^{-1}) for Monomeric and Oligomeric Species in Solutions of Hydrolyzed Ti(IV)

type of ligand	estimated value
oxo and hydroxo bridges	100 ± 50[a]
terminal OH$^-$ or H$_2$O	3400 ± 200[b]
TiO^{2+}	16 000 ± 5000[c]

[a] Assuming quadrupolar relaxation only; $k \approx {}^1/_3(1/T_2{}^b)$ at the minimum of the ln $(1/T_2{}^b)$ vs. $1/T$ function. [b] On the basis of a quadrupolar relaxation $1/T_{2Q}{}^b \approx 200$ s^{-1} (see oxo and hydroxo bridges); only limit for slowest exchanging terminal water and hydroxide ligands (see text). [c] Extrapolated by Eyring fit; measurements in 68% aqueous methanol.

Semiquantitative Analysis of Oxygen-Exchange Rates of Monomeric and Oligomeric Species. Oxygen-exchange rates have been measured by ^{17}O NMR fast-injection and line-broadening techniques. Ti(IV) in the solutions used is stable toward oxidation and reduction, and all reagents added were analytically pure. The fast-injection studies are limited by the time required to measure meaningful spectra (~50 scans; ~1.8 s/spectrum). Since all observed oxygens have already exchanged completely after the measurement of the first spectrum, only a lower limit for the exchange rates of yl-type oxygens, oxo and hydroxo bridges, and terminal H$_2$O and OH$^-$ ligands can be deduced from these experiments ($k_{\mathrm{ex}}{}^{298} < 2$ s^{-1}). The line-broadening measurements are limited by the temperature range: The upper limit is ~323 K (decomposition), and the lower limit is ~263 K for aqueous solutions (freezing) and ~183 K for methanol/water mixtures (line broadening caused by increasing viscosity).[59] In the slow-exchange limit the observed transverse relaxation rate $1/T_2{}^b$ of the coordinated oxygen atoms is related to $1/T_{2Q}{}^b$ (eq 8; *k* is the

$$1/T_2{}^b = k + 1/T_{2Q}{}^b \qquad (8)$$

exchange rate of a particular coordinated oxo ligand and $T_{2Q}{}^b$ is the quadrupolar relaxation rate). From the temperature dependence of $1/T_2{}^b$ it follows that at low temperature the line width

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(57) Oligomeric species are expected to exhibit vibrations in the region 500–900 cm^{-1}, depending on the type of oxo or hydroxo bridges involved.[58] Our experiments, however, have been performed under conditions ($[\mathrm{Ti(IV)}]_{\mathrm{total}} = 0.05$ *m*) where no such species are present.

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(59) In principle, it could be possible that the system also contains some very slowly exchanging oxygen atoms, which would not exchange during the preparation of the solutions and the time required for the ^{17}O NMR measurements and which therefore could escape observation. This could be ruled out by direct hydrolysis of TiCl$_4$ in enriched (^{17}O)water since these spectra are identical with the ones prepared as usual.

Table VI. Analysis of the Relaxation Rates $1/T_2^b$ of the Yl Oxygen of Monomeric Titanyl as a Function of [H$^+$] (T = 195.85 K; Numbering of Solutions as in Table I)

soln	[Ti(IV)], *m*	[TiO^{2+}], *m*	[H$^+$], *m*	$1/T_2^b \approx k_{ex}^{196}$,^{a} s^{-1}
25	0.0302	0.0042	0.9972	6600 ± 70
26	0.0302	0.0022	1.4789	7540 ± 70
27	0.0302	0.0012	1.9606	7850 ± 80

^{a} Fitted with Lorentzian functions.

is dominated by quadrupolar relaxation alone. When the kinetic term becomes dominant, the line width increases with temperature again. The slope of the high-temperature part of a plot of ln $(1/T_2^b)$ vs. $1/T$ is larger than that where $1/T_{2Q}^b$ is dominant (at the minimum of the ln $(1/T_2^b)$ vs. $1/T$ function k is usually about $^1/_3(1/T_2^b)$) since $E_a(k) > E_a(1/T_{2Q}^b)$.[60,61] Table IV shows the effect of temperature on the line widths of the various signals. Clearly, the line width of signals 1 and 7 (monomeric titanyl and terminal water or hydroxide of oligomers, respectively; it has to be noted that only the slowest exchanging terminal water and hydroxide ligands of oligomeric species have been observed; it is clear from an analysis of the integrals and from temperature-dependence studies that there are some additional fast-exchanging terminal water and hydroxide ligands, viz. the estimated rate given in Table V is only a lower limit) is governed largely by the kinetic term, whereas the line width of signals 2–6 (bridging oxo or hydroxo ligands) is governed mainly by quadrupolar relaxation. For the bridging oxo ligands it appears that at the highest temperature used (304.3 K) the minimum of the ln $(1/T_2^b)$ vs. $1/T$ function is reached, viz. on further increase of the temperature the line widths would increase again. The rates therefore can be estimated with reasonable accuracy. The exchange rates of terminal water and hydroxide and of TiO^{2+} at ambient temperature are estimated from the ^{17}O NMR relaxation rates (see Table IV) with an Eyring fit. The estimated exchange rates for all species are given in Table V.

Although the reported oxygen-exchange rates are only estimates, it is clear that all oxygens involved in the system of hydrolyzed Ti(IV) exchange very fast; viz., the whole system is very labile.[59] This is also in agreement with ion-exchange experiments. The whole amount of Ti(IV) charged on Dowex 50W-X2 resin is eluted with 1.0 M HClO$_4$ without any sign of separation, although oligomeric and highly charged particles are involved with certainty. This is not unexpected in terms of the lability of the system. However, we point out that great care should be taken in the interpretation of earlier results based on ion-exchange experiments of hydrolyzed Ti(IV).[14,37,39]

The fast-exchange rate of the yl oxygen in TiO^{2+} is somewhat unexpected (see Discussion). One possible reason for that result is that any protonated species (intra- or intermolecular), viz. Ti(OH)$_2^{2+}$, TiOH^{3+}, or Ti^{4+}(aq), might be responsible for the fast exchange (Scheme I). Since the $1/T_2^b$ value of TiO^{2+} is mainly governed by chemical exchange, we have analyzed its line width as a function of [H$^+$] (Table VI). Unambiguously, there is a small increase of the exchange rate with increasing [H$^+$]. It follows that there is possibly a pathway by some protonated species. However, the fact that the exchange rate of TiO^{2+} is in general unexpectedly high (we note that this observation is not restricted to the low-temperature measurements in methanol/water mixtures; it is also applicable to aqueous acidic Ti(IV) solutions at ambient temperature) cannot be fully explained by an intermolecular protonation of TiO^{2+} (see Discussion).

Discussion

Oligomers. Some Ti(IV) compounds forming polymeric –Ti–O–Ti–O– chains (e.g. TiOX$_2$, X = F, Cl, Br, I, (SO$_4$)$_{1/2}$[30]) or oligomeric rings (e.g. [TiO(C$_2$O$_4$)$_2^{2-}$]$_4$,[62] [TiO(nitrilotriacetate)$^-$]$_4$[32]) in the solid state have been known for some time. However, oligomers have not yet been studied in acidic aqueous solutions of Ti(IV), although it is well-known that Zr(IV) and Hf(IV) have a strong tendency to form oligomeric species.[63–66] Also, oligomerization and polymerization are known to occur for many transition-metal ions upon hydrolysis (e.g. Cr(III),[67,68] Mo^{n+} (n = 2–6),[7] W^{n+} (n = 4–6),[8,69] Fe(III)[70]). The presence of oligomers in acidic solutions of hydrolyzed Ti(IV) is clearly established in the present investigation. The ease of formation of oxo and hydroxo bridges to Ti(IV) clearly has some impact on concentration-dependent kinetic studies and on the question of inner- and outer-sphere electron-transfer processes involving Ti(IV), in particular where [Ti(IV)] is high, [H$^+$] is low, and ionic strengths are high.

It is shown unambiguously that up to five different oligomeric species exist in appreciable concentrations in aqueous solutions with 0.1 m < [Ti(IV)]$_{total}$ < 0.5 m, 1.0 m < [H$^+$] < 2.5 m, 2.3 m < μ < 4.0 m, and 263 K < T < 323 K. The amounts of additional oligomeric species present are ≲2.5% of [Ti(IV)]$_{total}$ (≲1% of the oligomers accounted for). The nuclearity of the oligomers is clearly determined by the concentration-dependence studies. However, the analysis of the number of different species, of their stoichiometries, and of their structures requires some assumptions. The concentration dependence of the ^{17}O NMR intensities reveals that the ratio of some bridging oxygens remains constant within the error (signals 3 and 6, signals 4 and 5; Figure 2). This might indicate that the signals are due to the same species. The constant ratio might, however, be accidental; viz., the formation constant of oligomers with the same nuclearity might be similar. We note, however, that the structural possibilities for oligomers with a given nuclearity are limited. It is unlikely, for example, that three different trimers are present. The best fit of our data is realized with a model consisting of two trimers (A and B) and one tetramer (C) (eq 9–11). The ^{17}O NMR signals

$$3\mathrm{TiO}^{2+} \rightleftarrows \mathrm{Ti_3O_4}^{4+} + 2\mathrm{H}^+ \qquad K_3^3 = 0.38 \pm 0.06 \tag{9}$$

$$3\mathrm{TiO}^{2+} \rightleftarrows \mathrm{Ti_3O^{\alpha}{}_3O^{\beta}{}_2H_3}^{5+} + \mathrm{H}^+ \qquad K_3^2 = 1.64 \pm 0.06\ m^{-1} \tag{10}$$

$$4\mathrm{TiO}^{2+} \rightleftarrows \mathrm{Ti_4O^{\alpha}{}_4O^{\beta}{}_2H_4}^{8+} \qquad K_4^1 = 2.31 \pm 0.03\ m^{-3} \tag{11}$$

are assigned as follows (Figures 1 and 2, Table I): signal 2, trimer A; signals 3 and 6, trimer B; signals 4 and 5, tetramer C. The proposed model is supported by the whole set of experimental data and by the fact that chemically reasonable structures may be proposed on this basis.

Of some concern is the fact that the model retained does not contain any dimeric species, although Ti(IV)–O–Ti(IV) clearly is a well-established structural unit. However (and apart from the quality of the fit), an inspection of the data (Table I, Figure 2) reveals that the dependence of the integrals of signals 4 and 5 on [Ti(IV)]$_{total}$ is clearly of a higher order than that of signals 2, 3, and 6, which all are similar in magnitude; viz., the nuclearity of the species responsible for signals 4 and 5 is larger than the nuclearity of the species responsible for signals 2, 3, and 6, which might be identical. There are two important points in relation to the fact that no dimeric species are observed: First, no *oligomeric* species containing some titanyl fragment are observed. This implies that monomeric titanyl is not a building block for oligomerization, and this might be the result of the lability of titanyl in general (see Results and below). Second, from the

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overall lability of the system it follows that only the thermodynamically stable species exist in solution; viz., in the limited ranges of $[H^+]$ and $[Ti(IV)]_{total}$ that are experimentally accessible the early stages of oligomerization might escape observation.

In conclusion we note that the formation of oligomeric species in acidic solutions of hydrolyzed Ti(IV) is firmly established. In addition, a set of stoichiometries can be proposed that is in agreement with all data presently available.

Monomers. The existence of monomeric titanyl has recently been established by Raman spectroscopy[40] and by EXAFS studies,[41] and it is further supported in the present study by FTIR spectroscopy, the chemical shift of the ^{17}O NMR signal for the yl oxygen, and its dependence on $[Ti(IV)]_{total}$.

Probably the most striking result is the lability of the yl oxygen. The extensively studied analogous $VO^{2+}(aq)$ ion exchanges its yl oxygen much more slowly. The exchange of vanadyl is by two pathways, i.e. a spontaneous and a base-catalyzed part (oxygen exchange rate $k_{obsd} = k_0 + k_{OH}K_a/[H^+]$ ($k_0 = 2.4 \times 10^{-5}$ s^{-1});[71] the coordinated water molecules are very labile, $k_{ex} = 5 \times 10^2$ and $\sim 10^9$ s^{-1} for equatorial and trans water ligands, respectively[72,73]). Titanyl exchanges its yl oxygen about 9 orders of magnitude faster than vanadyl (Table V; we do not have any quantitative information on the water-exchange rates of TiO^{2+}; however, it is reasonable to assume that they are comparable to the exchange rates of vanadyl), and this is an acceleration that certainly cannot be attributed to electronic effects alone. We therefore propose an oxygen-exchange mechanism that is different from the one established for vanadyl.

This can be substantiated by qualitatively adjusting the well-known Ballhausen and Gray MO scheme of VO^{2+}[2] to titanyl. The additional electron of the d^1 VO^{2+} cation lies in the nonbonding molecular orbital of b_2 symmetry (d_{xy}) and is therefore unlikely to affect the reactivity substantially. The change in overlap between the d orbitals of V(IV) and Ti(IV) and the oxygen orbitals is governed by two opposing trends. First, the 3d orbitals of Ti(IV) are less contracted than those of V(IV) (the ionic radius of V(IV) is smaller than that of Ti(IV); for d-orbital coefficients see ref 74). Second, the 3d orbitals of Ti(IV) are higher in energy than those of V(IV) (i.e. close to the energy of 4s orbitals, which remain roughly unchanged). An analysis of the relative bond strengths on this qualitative basis is not warranted. A comparison of structural and vibronic spectroscopic data of some titanyl compounds[33-36] with those of vanadyl[2-4,56,75] reveals, however, that the bond strengths of the two yl oxygens must be very similar. Another effect might be of some importance: The higher energy of the Ti(IV) 3d orbitals clearly leads to σ and π molecular orbitals that have more oxygen character than those of V(IV). This might imply that the titanyl oxygen has more electron density than in the case of vanadyl, and titanyl is therefore easier to protonate than vanadyl. This, in fact, is exactly what one observes: There is a $[H^+]$ dependence of the oxygen-exchange rate of titanyl (viz. the exchange rate increases with increasing $[H^+]$; see Results), whereas the exchange of the vanadyl oxygen is base-catalyzed (see above). The higher electron density of the titanyl oxygen compared to that of the vanadyl oxygen is also in qualitative agreement with the reduction potentials (VO^{2+}, $E_0 = 0.34$ V; TiO^{2+}, $E_0 = 0.03$ V). Electron-transfer kinetics also clearly indicate that titanyl may be protonated since the electron transfer of titanyl is acid-catalyzed whereas that of $Ti^{III}(aq)$ is base-catalyzed (i.e. $TiOH^{3+}$ is the intermediate of the self-exchange reaction).[29] For the various acidity constants (Scheme I) there are only estimates available: $K_{a3}^M = 2.0$[37] and $K_{a2}^M K_{a1}^M > 25$ ($K_{a2}^M < K_{a1}^M$; viz., the formation of the yl bond stabilizes TiO^{2+}).[28] Vanadyl, on the other hand, is practically not protonatable in aqueous solution.[76]

On the basis of $[H^+]$-dependent potentiometric titrations it was recently claimed that up to 3.0 M $[H^+]$ TiO^{2+} is the principal species in solution; viz., TiO^{2+} is not protonated under these conditions.[28] This is in contrast to our observations (we note that this remark is not based on the low-temperature ^{17}O NMR studies alone since the change in the medium might be too influential; however, the extremely fast exchange of the yl oxygen under conditions similar to those for the potentiometric study indicates that some inter- or intramolecular protonation of TiO^{2+} might occur under these conditions also). From a critical analysis of the published potentiometric data it follows that some protonation of TiO^{2+} might happen.[77] Preliminary $[H^+]$-dependent UV spectroscopy experiments have shown that at a reasonable ionic strength ($\mu = 3.0$ *m*) the amount of protonated species is too small to calculate the protonation constants with reasonable accuracy. An analysis of the data, however, seems to imply that $K_{a2}^M < K_{a1}^M$ (i.e., the second protonation of titanyl is easier than the first one), and it seems to be reasonable that the loss of stability by a protonation of the yl bond is more important than the charge effect.

We now turn to the species responsible for the fast exchange of the TiO^{2+} yl oxygen (Scheme I). On the basis of $K_{a2}^M < K_{a1}^M$ there appear to be two possible mechanisms to explain the enormous rate enhancement, viz. either the intramolecular protonation product $Ti(OH)_2^{2+}$ or the doubly protonated Ti(IV) aqua ion are the reactive species. An analysis of the low-temperature ^{17}O NMR studies in methanol/water mixtures in terms of the amount of TiO^{2+} present and its dependence on $[H^+]$ indicates that an appreciable amount of TiO^{2+} is protonated under these conditions. However, at ambient temperature in aqueous acidic solutions it is evident from potentiometric titrations[28] and spectrophotometric experiments that the concentration of protonated species is very low, indeed. Therefore, the increase of the oxygen-exchange rate of titanyl vs. that of vanadyl of about 9 orders of magnitude indicates that the acceleration caused by $Ti^{4+}(aq)$ would have to be significant with catalytic concentrations already, if protonated species were to be responsible for the fast exchange. The low-temperature studies (Table VI), however, indicate that the rate enhancement with increasing $[H^+]$ is rather small. Therefore, $Ti^{4+}(aq)$ cannot be the only reactive species and a $[H^+]$-independent pathway must be largely responsible for the fast exchange (eq 16). For methanol/water mixtures $k_0^{298} \approx$

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(77) The original model[28] involved eq 12 and a fit of the data to the Nernst equation (eq 13):

$$TiO^{2+} + 2H^+ + e^- \rightarrow Ti^{3+}(aq) + H_2O \qquad (12)$$

$$E([H^+]) = E_0 + 0.059n \log [H^+] \qquad (13)$$

If this model is correct, the slope *n* should be 2.0. The reported slope was 2. A repetition of the fitting procedure, however, revealed that there is a small but significant difference from 2 ($n = 1.79 \pm 0.05$). Even with a good fit, the model used therefore is not correct. Clearly, at 3.0 *m* Cl^- complexation of Ti(III) by Cl^- cannot be neglected and the low value of *n* might be the result of some chloro complex formation. The deviation of *n* from 2.0 might, however, also be the result of some protonation. If protonated species are added to the system (Scheme I), the fitting functions are either eq 14 ($TiO^{2+} + H^+ \rightleftarrows TiOH^{3+}$, K_{a2}^M) or eq 15 ($TiO^{2+} + 2H^+ \rightleftarrows Ti^{4+}(aq)$, $\beta = K_{a2}^M K_{a1}^M$):

$$E([H^+]) = E_0 + 0.059 \log \frac{[H^+]^2}{1 + \beta[H^+]} \qquad (14)$$

$$E([H^+]) = E_0 + 0.059 \log \frac{[H^+]^2}{1 + [H^+]^2} \qquad (15)$$

In view of the limited number of experimental data it is inappropriate to involve a model that fits the two protonation constants K_{a2}^M and K_{a1}^M separately. The fitted parameters are as follows: eq 13, $E_0 = 31 \pm 2$ mV, $n = 1.79 \pm 0.05$; eq 14, $E_0 = 40 \pm 5$ mV, $K_{a2}^M = 0.29 \pm 0.18$ M^{-1}; eq 15, $E_0 = 36 \pm 4$ mV, $\beta = K_{a2}^M K_{a1}^M = 0.057 \pm 0.055$ M^{-2}. Because of the limited number of experimental data and the limited pH range ($\mu = 3.0$ M; the curvature of the $E([H^+])$ vs. $[H^+]$ plots only starts at rather high $[H^+]$) and because the degree and effects of Cl^- complexation are not known quantitatively, no clear answer in terms of the protonation constants K_{a2}^M and K_{a1}^M can be given. The interpretation given in ref 28, however, that TiO^{2+} clearly is the only species in solution, viz. that no protonation occurs, is principally incorrect. Details of the fits are given in the supplementary material.[52]

$$k_{ex} = k_0 + k_H[H^+]^2 \qquad (16)$$

16 000 s^{-1} and $k_H^{298} \approx 2000$ m^{-2} s^{-1} are roughly estimated from the experimental data (Table VI). As discussed already, TiO^{2+} is not likely to be responsible for the k_0 term in eq 16. Since the equilibrium between TiO^{2+} and $Ti(OH)_2^{2+}$ is [H$^+$]- and [Ti(IV)]$_{total}$-independent, the equilibrium constant remains unknown. On the basis of the stability of the TiO^{2+} yl bond it, however, seems to be unlikely that the concentration of $Ti(OH)_2^{2+}$ is large. This might be one reason for the fact that the dihydroxo species still has escaped any direct experimental proof.

We conclude that our results together with earlier work indicate that monomeric titanyl exists in aqueous acidic solution. The fact that TiO^{2+} exchanges its oxygen very fast is explained by a relatively easily protonated yl oxygen. This clearly indicates that monomeric titanyl is in equilibrium with other monomeric species, which most probably include $Ti(OH)_2^{2+}$ and Ti^{4+}(aq).

Acknowledgment. We are grateful to Dr. F. P. Rotzinger (EPF Lausanne) for the donation of a sample of purified and analyzed $TiOSO_4 \cdot 2H_2O$ and to Dr. R. Humphry-Baker (EPF Lausanne, light scattering), Dr. L. Helm (Universitê de Lausanne, NMR), E. Cotelioglu (Universitê de Lausanne, computing), and V. Kasparek and C. Desponds (Universitê de Lausanne, FTIR) for their help with the instrumentation. We thank the Swiss National Science Foundation for financial support through Grant 2.854-0.85.

Registry No. TiO^{2+}, 12192-25-5; Ti, 7440-32-6; oxygen, 7782-44-7.

Supplementary Material Available: Details of the oligomer fits, listings of calculations on the potentiometric titrations, and details of the pK_a determinations (19 pages). Ordering information is given on any current masthead page.

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Absorption Spectra, Electrochemical Behavior, Luminescence Spectra, and Excited-State Lifetimes of Mixed-Ligand Ortho-Metalated Rhodium(III) Complexes

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Received July 25, 1986

We report results of an investigation on the absorption spectra, electrochemical behavior, luminescence spectra, and excited-state lifetimes of the $Rh(phpy)_2(bpy)^+$ and $Rh(thpy)_2(bpy)^+$ complexes, where phpy$^-$ and thpy$^-$ are the ortho-C-deprotonated forms of 2-phenylpyridine and 2-(2-thienyl)pyridine and bpy is 2,2′-bipyridine. The results obtained have been compared with those previously available for $Rh(bpy)_3^{3+}$ and for Pt(II) and Pt(IV) complexes containing the phpy and thpy ligands. On electrochemical oxidation, the two mixed-ligand complexes exhibit an irreversible wave at about +1.1 V and, on reduction, a reversible one-electron wave at −1.4 V. Besides ligand-centered bands in the UV region, the absorption spectra of the mixed-ligand complexes show intense bands at lower energy (λ_{max} = 367 nm for $Rh(phpy)_2(bpy)^+$ and 379 nm for $Rh(thpy)_2(bpy)^+$ that are assigned to metal-to-ligand (presumably, Rh → phpy$^-$ and Rh → thpy$^-$) charge-transfer transitions. Both complexes exhibit a strong and long-lived ($\tau \approx$ 0.17 and 0.50 ms for $Rh(phpy)_2(bpy)^+$ and $Rh(thpy)_2(bpy)^+$, respectively) luminescence emission at 77 K in rigid matrix, which is assigned as a triplet ligand-centered luminescence of the phpy$^-$ and thpy$^-$ ligands. For $Rh(phpy)_2(bpy)^+$, there is indication of some mixing of the emitting triplet ligand-centered state with a charge-transfer state. Emission lifetime and emission intensity decrease strongly in fluid solution. For $Rh(phpy)_2(bpy)^+$, no emission can be observed above 222 K, whereas $Rh(thpy)_2(bpy)^+$ is luminescent even at room temperature (τ = 1.0 μs). The results obtained, compared with those available for $Rh(bpy)_3^{3+}$, are consistent with a higher ligand field strength of the ortho-metalated ligands compared with that of bpy. Because of its redox and luminescence properties, $Rh(thpy)_2(bpy)^+$ promises to be a useful excited-state reactant and excited-state product in electron-transfer reactions.

Introduction

In the search for new luminescent compounds that can play the role of light absorption and/or light emission sensitizers,[4] we have studied the photophysical and photochemical properties of several Ru(II) diimine complexes.[5] Recently, we have extended our interest to ortho-metalated complexes that contain ligands similar to diimines and exhibit very interesting excited-state properties. Results concerning ortho-metalated Pt(II)[6] and Pt(IV)[7] complexes have already been presented.

In this paper, we report the results of an investigation on the $Rh(phpy)_2(bpy)^+$ and $Rh(thpy)_2(bpy)^+$ complexes, where phpy$^-$ and thpy$^-$ are the ortho-C-deprotonated forms of 2-phenylpyridine and 2-(2-thienyl)pyridine and bpy is 2,2′-bipyridine (Figure 1). The results obtained have been compared with those previously available for $Rh(bpy)_3^{3+}$. Studies on the dichloro-bridged dimeric $[Rh(phpy)_2Cl]_2$ complex[8a] and on dimeric[8a] and monomeric[9,10]

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