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Electron Transfer. 77. Electrochemistry of Carboxylato-Bound Chromium(V)[1a]

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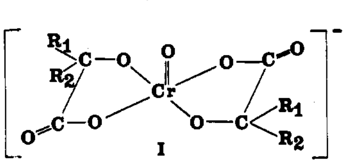
The chelated chromium(V) complex sodium bis(2-ethyl-2-hydroxybutyrato)oxochromate(V) (I) undergoes quasi-reversible 1e redox in aqueous perchlorate in the pH range 3.5–6.0. The reduction potential for the Cr(V)/Cr(IV) redox couple is 0.19 V vs. SCE and is independent of [H$^+$] in this pH range. The electrode process is coupled with a slow irreversible chemical reaction due to the reduction of the chromium(IV) species by the hydroxycarboxylic acid to form Cr(III) and 3-pentanone. The bis chelate equilibrates with a monochelated species with an equilibrium constant associated with the process $L_2Cr^V(O) + H^+ \rightleftharpoons LCr^V(O) + LH$ (where LH represents 2-ethyl-2-hydroxybutyric acid), estimated to be (4 ± 2) × 10^{-3}. In the acidity range 0.01–0.1 M, the chromium(V) chelate undergoes a proton-assisted 2e irreversible reduction directly to form chromium(III) products.

Introduction

Since the discovery of water-soluble stable carboxylato chromium(V) complexes[2] (I), redox and mechanisms involving these complexes with various organic and metal reductants have been reported from this laboratory.[3-8] Reductions of these Cr(V) complexes, especially by 1e reductants, may proceed through Cr(IV). The chemistry for this still less usual oxidation state is largely unknown. Iron(II) and vanadium(IV) reductions of bis(2-ethyl-2-hydroxybutyrato)oxochromate(V) (I, $R_1 = R_2 = C_2H_5$) in aqueous solution proceed through an intensely absorbing intermediate whose spectral and EPR properties are consistent with formulation as a complex of chromium(IV).[6,7] The formation of a few oxochromium(IV)[9,10] complexes of various porphyrin ligands and some alkoxide complexes of Cr(IV)[11] have been reported in nonaqueous solvents; rapid decomposition in contact with moisture complicates further studies on these systems. The present report deals with the electrochemical properties of chromium(V)/chromium(IV) and chromium(V)/chromium(III) redox couples in aqueous perchlorate media in the pH range 1–6; our findings should add detail to our picture of the redox mechanisms involving Cr(V) and Cr(IV).


I

Experimental Section

Physical Measurements. Ultraviolet–visible spectra were recorded on a Beckman 5260 spectrophotometer. Cyclic voltammetry measurements were performed on a Princeton Applied Research (PAR) Model 173 potentiostat/galvanostat in conjunction with a Model 175 universal programmer as a sweep generator. The voltammograms were recorded on a X–Y recorder by connecting it with a logarithmic current converter (PAR Model 376). The magnitude of *iR* drop across the working and reference electrodes was minimized by the use of a positive feedback *iR* accessory of the current converter. Traces of voltammograms using faster scan rates (0.5 V^{-1} and higher) were displayed on an oscilloscope (Tektronix Type 549 Storage Oscilloscope) and pictures were taken with a Polaroid camera. A conventional H-type cell was generally used for electrochemical measurements. In some measurements a specially designed three-electrode cell coupled with a Luggin capillary was used. All the measurements were performed by utilizing a three-electrode system such as a glassy-carbon (working), a calomel (reference), and a platinum-wire (auxiliary) electrode. The partial electrolysis of the chromium(V) complex was accomplished by a graphite porous block working electrode, keeping the potential constant at 0.3 V negative to the cathodic peak potential. The ionic strength was maintained at 1.0 M with $LiClO_4$. Unless otherwise stated, solutions were unbuffered, and pHs were adjusted with dilute perchloric acid or sodium hydroxide. The pH values were checked on a pH meter (Orion Model 601/Ionalyzer) before and after measurements. Gas chromatograms were recorded on a Varian Model 3700 Gas Chromatograph using a flame ionization detector.

Materials. Sodium bis(2-ethyl-2-hydroxybutyrato)oxochromate(V) was synthesized as a monohydrate following the method of Krumpolc and Roček[2] and was recrystallized from acetone–chloroform.[7] Lithium perchlorate was prepared by the method of Dockal[12] and recrystallized twice before use. The carboxylic acid, 2-ethyl-2-hydroxybutyric acid (Aldrich) was recrystallized from *n*-hexane. 3-Pentanone (Baker) was used as received. Stock slutions of oxovanadium(IV) perchlorate and europium(III) perchlorate were prepared according to methods described earlier.[7,13]

Methods. The $E_{1/2}$ values were calculated from the arithmetic mean of the cathodic and anodic peak potentials and are reported with respect to saturated calomel electrode. The anodic and cathodic peak currents ($i_{p,a}$ and $i_{p,c}$) were determined according to the method of Nicholson.[14] For the totally irreversible cyclic voltammograms, the values of αn_a, were calculated from the peak potentials by using the expression[15]

$$E_p - E_{p/2} = 1.857RT/\alpha n_a \qquad (1)$$

where E_p and $E_{p/2}$ are the potentials at currents i_p and $i_p/2$, n_a is the number of electrons transferred in the rate limiting step, and α is the coefficient of electron transfer. The value of n, the number of electrons involved in the redox process, was calculated from[15]

$$i_p = (2.99 \times 10^{-5})n(\alpha n_a)^{1/2}AC_0D_0^{1/2}v^{1/2} \qquad (2)$$

where A is the surface area of the electrode (cm^2), D_0 is the diffusion coefficient (cm^2 s^{-1}), C_0 is the bulk concentration of the substrate (mol cm^{-3}), and v is the sweep rate (V s^{-1}). The diffusion coefficient was estimate from the current–time curves[16] obtained at a potential at least 0.3 V cathodic to the reduction waves for the quasi-reversible processes. No attempt was made to estimate the diffusion coefficient for the substrate, where a totally irreversible electrode process was observed.

The equilibrium constant for the loss of ligand

$$L_2Cr^V(O) + H^+ \rightleftharpoons LCr^V(O) + LH \qquad (3)$$

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(16) (a) Current–time profiles were monitored at three different potentials, –0.2, –0.3, and –0.4 V vs. SCE for the solution containing 0.2 mM Cr(V) complex in 1.0 M $LiClO_4$. The diffusion coefficient was estimated from the slope of plots of current *vs.* $t^{1/2}$. The diffusion coefficient obtained for the Cr(V) dichelate was (6 ± 1) × 10^{-6} cm^2 s^{-1}. See, for example: Reference 15; pp 142, 233.

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Table I. Electrochemical Data[a] for Reduction of Bis(2-ethyl-2-hydroxybutyrato)oxochromate(V)[b] in 1.0 $LiClO_4$ in the pH Range 2.5–6.0

pH	scan rate, V s^{-1}	$E_{p,c}$(A), V	$E_{p,a}$(B), V	ΔE_p, mV	$E_{1/2}$, mV	i_a/i_c	$E_{p,c}$(C), V
6.0	0.10	0.135	0.250	115	0.193	1.02	−0.05
5.0	0.01	0.155	0.225	70	0.190	0.84	0.00
5.0	0.10	0.130	0.250	120	0.190	1.03	−0.04
4.1	0.01	0.158	0.228	70	0.193	0.79	0.01
4.1	0.02	0.154	0.238	84	0.196	0.89	0.00
4.1	0.05	0.150	0.242	92	0.196	1.02	−0.01
4.1	0.10	0.134	0.248	114	0.191	1.03	−0.03
4.1	0.50	0.127	0.266	139	0.196	1.02	−0.05
4.1	1.00	0.111	0.273	162	0.192	1.07	−0.07
3.5	0.01	0.156	0.228	72	0.192	0.81	0.00
3.5	0.10	0.130	0.245	110	0.188	0.98	−0.04
2.5	0.01	0.250				<0.40	0.00
2.5	0.05	0.217	0.292	75	0.255	0.44	−0.03
2.5	0.10	0.193	0.298	115	0.246	0.50	−0.05
2.5	0.5	0.178	0.327	149	0.253	0.50	−0.08

[a] Potentials are with reference to SCE and are within ±4 mV. [b] The concentrations of the chromium(V) species were in the range 1.5–2.5 mM; (A), (B), and (C) refer to the peaks A, B, and C described in the text.

was estimated from the peak current of the respective chromium(V) species. The current of the first peak was determined with reference to the base line of the electrolyte itself. The base line for the second peak was established by stopping the sweep at a potential 120 mV negative to the first peak. The current slowly dropped to a small value, and this small current level was then treated as the base line for the second component. The peak current was then measured with reference to this base line by resuming the sweep.[16] The concentrations of the dichelate (I) and monochelate were obtained from

$$[L_2Cr^V(O)] = i_p/(i_p + i_p') \qquad (4)$$

$$[LCr^V(O)] = i_p'/(i_p + i_p') \qquad (5)$$

where i_p and i_p' are the peak currents from the dichelate and the monochelate, respectively.

Examination of Electrolyzed Products. A solution of the chromium(V) complex (5×10^{-3} M; 15 mL) in 1.0 M $LiClO_4$ was electrolyzed at −0.3 V vs. SCE by using a rectangular graphite bar as a working electrode at pH 4. After 2 h of electrolysis, the solution exhibited two shoulders at 565 and 410 nm in addition to the 510-nm band due to the starting Cr(V) complex. The remaining concentration of Cr(V) (2.5×10^{-3} M) was estimated spectrophotometrically.[17] The solution containing the reactant and the products was passed through an anion-exchange column (Bio-Rad Ag X-2; Cl^- form; 4 mequiv) to remove the remaining starting material. The pale green eluate exhibited bands at 565 nm ($\epsilon = 19$ M^{-1} cm^{-1})[18a] and 412 nm ($\epsilon = 35$ M^{-1} cm^{-1}),[18b] indicating a chromium(III) spectrum.[19] In the electrolyzed solution, the presence of CrO_4^{2-} was not observed.[18c] A blank experiment using the same Cr(V) concentration without electrolysis was carried out, and it was observed that 1.0×10^{-3} M Cr(V) was decomposed[20] during the time ordinarily used for electrolysis.

Aliquots of the eluate were subjected to gas chromatography, and 3-pentanone was detected. An estimate of the amount of ketone (against a standard sample) yielded about 1×10^{-3} M. An experiment with a blank sample under identical conditions yielded 2×10^{-4} M ketone. The amount of ketone estimated in the electrolyzed solution at pH 1.0 (rather than pH 4) was approximately the same as observed in the blank sample.

Results and Discussion

The cyclic voltammograms of the chromium(V) chelate (I) on a glassy-carbon electrode exhibit two reduction waves[21] (A and C), of which one shows an anodic return wave (B) in the potential range +1.0 to −0.5 V (pH 3.5–6.0). Figure 1 shows the voltammogram at pH 4.1. A separation of 70 mV between the cathodic and anodic waves, A and B, was observed at a sweep rate of 10 mV s^{-1}. Peak separations increase with increasing scan rates.[22] The ratio of the peak currents for these two redox waves (A and B) was found to be 1.02 ± 0.03 in the range of scan rates 0.05–2 V s^{-1}. At lower scan rates the above ratio falls below unity due to an irreversible chemical reaction following the charge-transfer process (see below). The above results are consistent with an explanation that waves A and B correspond to a quasi-reversible 1e, Cr^V/Cr^{IV}, redox process. The possibility that peaks A and B arise from a 2e redox couple of highly irreversible nature can be ruled out from the fact that the voltammogram of chemically reduced chromium(III) species (generated from Cr(V) by Eu^{2+} reduction)[7] does not show any anodic wave in the potential range studied.

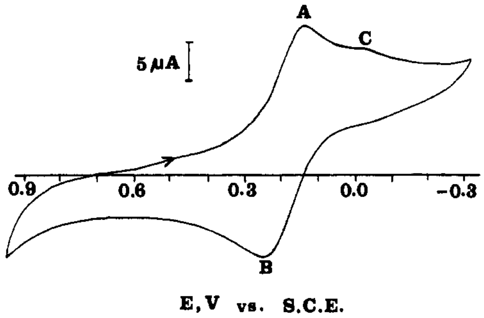

Figure 1. Cyclic voltammogram of bis(2-ethyl-2-hydroxybutyrato)oxochromate(V) (2.4×10^{-3} M) in 1.0 M $LiClO_4$ at pH 4.1 using a 0.1 V s^{-1} sweep rate. Peaks A and B correspond to a quasi-reversible 1e Cr(V)/Cr(IV) redox couple. The reduction peak C arises from a monochelated (hydroxycarboxylato)chromium(V) due to the loss of a ligand from the bis chelate (see text).

The remaining reduction wave, C, for which no return anodic wave was observed, appears as a small shoulder about 150 mV cathodic to wave B. The cathodic wave, C, cannot be due to the further reduction of Cr^{IV} to Cr^{III}, for if it were, the peak current should be much higher. When the voltammograms were recorded in the presence of added 2-ethyl-2-hydroxybutyrate buffer (0.01 M sodium salt and acid, pH 3.3) peak C completely disappeared.

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(17) The bis(carboxylato)chromium(V) chelate exhibits a shoulder at 350 nm ($\epsilon = 1.2 \times 10^3$ M^{-1} cm^{-1}) whereas Cr(III) species absorb negligibly at this wavelength.

(18) (a) For the estimation of extinction coefficients of the chromium species present in the eluate, aliquots of eluted fraction were oxidized with basic H_2O_2 and the total chromium content was determined as chromate. (See, for example: Haupt, G. W. *J. Natl. Bur. Stand., Sect. A* **1952**, *48*, 414). (b) The relatively high extinction coefficient at 410 nm, as compared to that at 565 nm, is probably due to the presence of a small amount of the chromium(V) complex passing through the resin. (c) Tests for chromate were done by adding $Ba(ClO_4)_2$ solution.

(19) The various carboxylato complexes of Cr(III) have absorption maxima with comparable extinction coefficients in the wavelength region observed here. See, for example: Butler, R. D.; Taube, H. *J. Am. Chem. Soc.* **1965**, *87*, 5597. Ward, J. R.; Haim, A. *J. Am. Chem. Soc.* **1970**, *92*, 475. See also ref 10.

(20) The starting Cr(V) complex undergoes a slow disproportionation reaction at this pH to form Cr(III) and Cr(VI) products.[2,3]

(21) In addition to these reduction waves, another shoulder appeared at 0.33 V at pH 3.5–5.0 for the first cycle; this shoulder disappeared in subsequent cycles. In this pH range the voltammograms obtained by using either gold or platinum rather than glassy carbon as the working electrode exhibit the same two cathodic waves (A and C), but no anodic return.

(22) Since the magnitude of the peak separations did not diminish when a Luggin capillary was used, we rule out the possibility that the separations are due solely to uncompensated solution resistance. Moreover, the present investigation was carried out in aqueous solution maintaining an ionic strength of 1.0 M, and resistance can be taken to be very small.

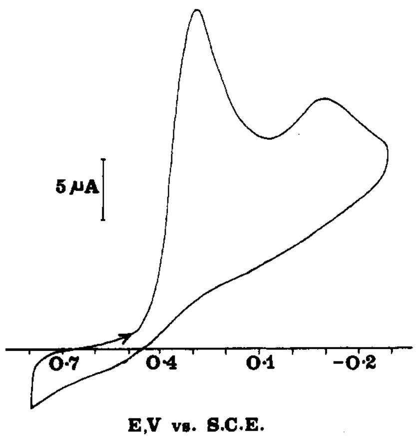


Figure 2. Cyclic voltammogram of bis(2-ethyl-2-hydroxybutyrato)oxochromate(V) 1.4 × 10^{-3} M) in 1.0 M $LiClO_4$–$HClO_4$ ($[H^+]$ = 0.01 M) using a 0.1 V s^{-1} sweep rate. Note that the voltammogram is totally irreversible, whereas at pH 4.1 quasi-reversible behavior for the dichelate was observed.

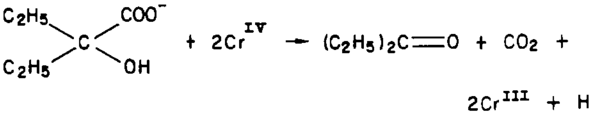
This is consistent with the formulation of an equilibrium involving the original dichelate and a monochelated species (see below). Wave B corresponds to the reduction of the original dichelate, I, whereas peak C is attributed to the reduction of the other equilibrated form, the monochelate.

Table I lists the peak potentials (E_p), their separations (ΔE_p), $E_{1/2}$, and the ratio of anodic to cathodic peak currents ($i_{p,a}/i_{p,c}$). The gradual increase in the ratios of peak currents with increasing scan rate is indicative of the occurrence of an irreversible chemical reaction following a quasi-reversible charge-transfer step. Since the current ratio approaches unity at a modest scan rate (0.05 V s^{-1}), the chemical reaction must be slow. Our data then allow us to suggest the overall scheme involving the predominant dichelate species as

$$L_2Cr^V(O) + H^+ \overset{K}{\rightleftharpoons} LCr^V(O)(H_2O) + LH \qquad (6)$$

$$L_2Cr^V(O) + e^- \xrightleftharpoons{E\,=\,0.19\text{ V}} L_2Cr^{IV}(O) \xrightarrow{\text{slow}} \text{products} \qquad (7)$$

The products of the reactions are identified as Cr(III) species and 3-pentanone. A stoichiometric conversion of Cr(V) to Cr(III) was observed. The quantity of the ketone obtained was one-half of [Cr(III)]. The Cr(IV) species was thus reduced chemically by the hydroxycarboxylic acid (eq 8). Reductions of Cr^{VI} and



$$(C_2H_5)_2C(COO^-)(OH) + 2Cr^{IV} \rightarrow (C_2H_5)_2C{=}O + CO_2 + 2Cr^{III} + H^+ \qquad (8)$$

Cr^{IV} (assumed to be a transient intermediate in some reductions of Cr^{VI}) by various hydroxycarboxylic acids to form ketones and Cr(III) species have been reported by Roček and co-workers.[23,24] The observed stoichiometry is consistent with one of the several mechanisms of reduction proposed by these authors.[23,24]

The rates of the chemical reaction can, in principle, be calculated from the various electrochemical parameters.[25-27] Since the electrode process is a quasi-reversible one, the system at hand falls in the KG domain[27] where the overall process is controlled by rates of both the electrode[28] and chemical reactions. Under these conditions, especially for the KG domain, calculation of the rate of chemical reaction using electrochemical data requires a rigorous computation. Since we can generate Cr(IV) species chemically, detailed mechanistic studies dealing with the decomposition of this species are being studied instead by conventional methods.[29]

Table II. Equilibrium Constant for the Proton-Assisted Ligand Loss from Bis(2-ethyl-2-hydroxybutyrato)oxochromate(V) (22 °C in 1.0 M $LiClO_4$)

$[H^+]$,[a] M	$[Cr^V]$, mM	$[L_2Cr^V(O)]$,[b] mM	$[LCr^V(O)]$,[b] mM	10^3K
0.01	1.40	1.14	0.26	6
0.05	2.0	1.46	0.54	4
0.10	1.80	1.12	0.68	4
0.10	1.40	0.89	0.51	3

[a] The acidity was maintained by adding $HClO_4$. [b] Concentrations of dichelate and monochelate were calculated by using eq 4.

Table III. Electrochemical Data for the Reduction of Bis(2-ethyl-2-hydroxybutyrato)oxochromate(V) (1.0 M $LiClO_4$, 0.01–0.1 M $[H^+]$, 22 °C)

$[H^+]$, M	scan rate, V s^{-1}	E_p,[a] V	E_p',[a] V
0.01	0.01	0.28	−0.08
0.01	0.02	0.27	−0.08
0.01	0.05	0.24	−0.10
0.01	0.10	0.23	−0.11
0.05	0.02	0.33	0.0
0.05	0.05	0.27	−0.02
0.10	0.01	0.36	−0.02
0.10	0.10	0.30	−0.02

[a] E_p and E_p' refer to the peak potential for the reduction wave of the dichelate and monochelate, respectively.

The apparent irreversibility of peak C may be due either to the quasi-reversible 1e transfer process followed by a faster irreversible chemical reaction, or to the completely irreversible 2e redox process to form a Cr(III) product directly. Since the current associated with this peak is small (due to the very small equilibrium concentration of this species as indicated below), a determination of the *n* value was not possible in the pH range 3.0–5.0 and, therefore, a choice between the processes cannot be made.

Apart from the sweep rates, the ratio of the anodic to cathodic peak currents (A and B) also depends upon the pH of the solution. For example, at pH 2.5, the peak ratio was observed to be 0.5 at a scan rate of 0.1 mV s^{-1}, and no appreciable increase in the ratio was observed up to a sweep rate of 0.5 V s^{-1}. When the pH of the solution is further lowered to 2.0, the voltammograms exhibit only two irreversible reduction waves up to scan rate of 2 V s^{-1}. Figure 2 shows a voltammogram at pH 2.0. The peak currents for both the waves increase linearly with the square root of the sweep rate. Cathodic shifts in the peak potentials with increasing scan rate were observed. The reduction current for peak C increases with increasing hydrogen ion concentration, consistent with equilibrium 3. The equilibrium constant, *K*, obtained at three different hydrogen ion concentrations is listed in Table II.[30] In a recent study dealing with the decomposition of carboxylato complexes of chromium(V) such an equilibrium has been suggested by Krumpolc and Roček.[31] However, no quantitative measurement on the equilibrium constant was reported by these authors.

In acidic solution in the pH range 1–2, the possibility of irreversibility due to the fast subsequent chemical reaction can be ruled out by the fractional limiting peak current ratio, 0.5 (at pH 2.5), which was observed at sweep rates 0.1–0.5 V s^{-1}. A monotonous increase in the peak current ratio up to unity is expected for the irreversible chemical reaction following the charge transfer on the electrode surface. Taking into consideration the equilibrium

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(27) Nadjo, L.; Saveant, J.-M. *J. Electroanal. Chem. Interfacial Electrochem.* **1973**, *48*, 113.
(28) If we consider the peak separation to be due mainly to sluggish electron transfer on the electrode surface,[14] the rate constant for the heterogeneous electron-transfer step can be calculated as (5 ± 2) × 10^{-3} cm^{-2} s^{-1}.
(29) Bose, R. N.; Gould, E. S., work in progress.
(30) In this pH range it is assumed that the coordinated hydroxyl oxygen is protonated. If we suppose a ligand dianion and use two protons (rather than one) in the stoichiometric eq 3, the equilibrium constants calculated at different pHs are found to vary by more than an order of magnitude.
(31) Krumpolc, M.; Roček, J. *Inorg. Chem.* **1985**, *24*, 617.

concentration of the two chromium(V) chelates, the number of electrons transferred corresponding to both peaks was calculated[32] to be 2 in the acidity range 0.1–0.01 M. Moreover, with an identical concentration, the integrated area of the cathodic portion of the curve was found to be 1.8 times higher at pH 2.0 than at pH 4.0. Table III summarizes the electrochemical data in the pH range 1–2. In acidic solution the electrode processes then can be represented by

$$L_2Cr^{V}(O) + 2H^+ + 2e^- \xrightarrow{\text{irreversible}} L_2Cr^{III}(H_2O) \quad (9)$$

$$LCr^{V}(O) + 2H^+ + 2e^- \xrightarrow{\text{irreversible}} LCr^{III}(H_2O) \quad (10)$$

The reduction waves for both species shift anodically with increasing hydrogen ion concentrations, in accord with our picture. From the dependence of reduction potential on pH, the number of protons involved in the redox process can, in principle, by calculated. Assuming that the rate of electron transfer does not change with pH, an anodic shift of 60 mV is expected for the reduction peak potentials of both the mono and dichelate for a 10-fold increase in the hydrogen ion concentration. We note that at a constant scan rate (0.1 V s^{-1}) the reduction wave for the dichelate shifted 70 mV in the positive direction when $[H^+]$ is increased from 0.01 to 0.1 M. Likewise, a slightly higher anodic shift (90 mV) was observed for the reduction wave of the monochelate for a 10-fold increase in $[H^+]$.

The reason for the irreversibility of the Cr(V)/Cr(III) couple is open to question. The irreversibility may be due to the marked structural differences associated with these two oxidation states. Another possiblility is that in acidic solution ($[H^+]$ = 0.01–0.1 M) the released hydroxycarboxylic acid may modify the electrode surface such that the reduced species is electroinactive. This view may be supported by the presence of only a single reduction peak in voltammograms obtained in the hydroxycarboxylate buffer (pH 3.5) whereas a quasi-reversible behavior was observed in the unbuffered solution having identical pH. We await further evidence before choosing between these alternatives.

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Registry No. I^-, 84622-43-5; $L_2Cr^{IV}(O)$, 99495-02-0; $LiClO_4$, 7791-03-9; $(C_2H_5)_2C{=}O$, 96-22-0.

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(32) In this calculation it is assumed that the value of the diffusion coefficient of the Cr(V) complexes does not change significantly with changing pH and that the diffusion coefficient of the monochelate is not much different from that of the bis chelate.

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Direct Synthesis of Alkali-Metal and Ammonium Pentafluoroperoxytitanates(IV), $A_3[Ti(O_2)F_5]$, and First Synthesis and Structural Assessment of Alkali-Metal and Ammonium Difluorodiperoxytitanates(IV), $A_2[Ti(O_2)_2F_2]$

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Yellow alkali-metal and ammonium pentafluoroperoxytitanates(IV), $A_3[Ti(O_2)F_5]$ (A = Na, K, NH_4), have been synthesized directly from the reaction of TiO_2 in 40% HF with 30% H_2O_2 at pH 6 maintained by the addition of the corresponding alkali metal or ammonium hydroxide. Novel alkali-metal and ammonium difluorodiperoxotitanates(IV), $A_2[Ti(O_2)_2F_2]$ (A = K, NH_4), have been synthesized from the reaction of a solution of TiO_2 in 40% HF with 30% H_2O_2 at pH 9 maintained by the addition of the corresponding AOH, followed by precipitation with ethanol. The compounds are all diamagnetic and permit molar conductance measurements. The IR and laser Raman spectra suggest that the peroxide groups are bonded to the Ti^{4+} center in a triangular bidentate (C_{2v}) manner and that ν_{O-O} decreases with the increase in the number of coordinated peroxide groups.

There has been a considerable recent interest in metal complexes that contain peroxide.[1,2] Some of this interest originates from the probable biochemical significance of peroxymetal complexes[1,3] and the potential use of hetero ligand peroxymetal compounds containing macrocyclic ligands as models for biological systems.[3] Our interest in this area stems from developing suitable methods of syntheses and making assessment of structures of hetero ligand peroxymetal compounds. We have embarked on a research program designed to find suitable methods for syntheses. Within the context of the present work there are certain aspects of the chemistry of peroxytitanates(IV), as reported in the literature,[4,5] that remain unclear. Notably important among them are the lack of a direct method for synthesizing alkali-metal and ammonium pentafluoroperoxytitanates(IV), $A_3[Ti(O_2)F_5]$, and the absence of any reported existence of difluorodiperoxytitanate(IV) complexes, $A_2[Ti(O_2)_2F_2]$. Reported in this paper are a direct general method for the synthesis of $A_3[Ti(O_2)F_5]$ (A = Na, K, NH_4), and the synthesis, characterization, and assessment of structure of novel hetero ligand peroxytitanate(IV) compounds of the type $A_2[Ti(O_2)_2F_2]$ (A = K, NH_4), and also a set of internally consistent data concerning the effect on ν_{O-O} modes with the increase in number of such groups coordinated to the Ti^{4+} center in going from $[Ti(O_2)F_5]^{3-}$ to $[Ti(O_2)_2F_2]^{2-}$. The syntheses have been achieved by conducting the reactions under two different, in each case specific, pH conditions.

Experimental Section

The chemicals used were all reagent grade products. IR spectra were recorded on a Perkin-Elmer Model 983 spectrophotometer. Laser Raman (LR) spectra were recorded on a Spex Ramalog Model 1402 spectrometer. The 4880-Å laser line from the Spectra-Physics Model 165 argon laser was used as the excitation source. The scattered light at 90° was detected with the help of a cooled RCA 31034 photomultiplier tube followed by a photon-counting processing system. The sample was held either in a quartz capillary or in the form of a pressed pellet, unless otherwise stated, and the spectra were recorded at ambient temperatures. Molar conductance measurements were made in aqueous solution with a Philips PR 9500 conductivity bridge. The pH of the reaction solutions was measued with a Systronics Type 335 digital pH meter and also with pH indicator (BDH) paper.

Synthesis of Alkali-Metal and Ammonium Pentafluoroperoxytitanates(IV), $A_3[Ti(O_2)F_5]$ (A = Na, K, NH_4). In a typical reaction, to a stirred cold solution of 2.0 g (25 mmol) of TiO_2 in 20 cm^3 (400 mmol) of 40% hydrofluoric acid, obtained by heating the mixture for ca. 20 min,

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