lutidine), 94483-34-8; $Fe(TPC)(L)_2$ (L = 3,4-lutidine), 94483-46-2; $Fe(TPC)(L)_2^+$ (L = 4-(dimethylamino)pyridine), 94483-35-9; $Fe(TPC)(L)_2$ (L = 4-(dimethylamino)pyridine), 94483-47-3; $Fe(TPC)(L)_2^+$ (L = *m*-nitroaniline), 94483-36-0; $Fe(TPC)(L)_2$ (L = *m*-nitroaniline), 94483-48-4; $Fe(TPC)(L)_2^+$ (L = aniline), 94483-37-1; $Fe(TPC)(L)_2$ (L = aniline), 94483-49-5; $Fe(TPC)(L)_2^+$ (L = benzylamine), 94483-38-2; $Fe(TPC)(L)_2$ (L = benzylamine), 94483-50-8; $Fe(TPC)(L)_2^+$ (L = piperidine), 94483-39-3; $Fe(TPC)(L)_2$ (L = piperidine), 94483-51-9.

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Chromium(V) Oxidations of Organic Compounds[1]

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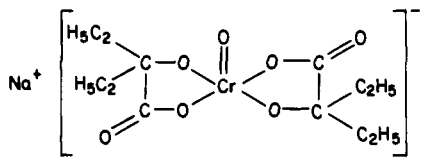
Sodium bis[2-ethyl-2-hydroxybutanoato(2−)]oxochromate(V) is sufficiently stable in aqueous solutions in the pH range 3–4 to allow the study of the oxidation of a series of organic substrates. Oxalic acid, primary and secondary 2-hydroxy acids, and 2-oxo acids react rapidly at 25 °C while for tertiary 2-hydroxy acids, alcohols, aldehydes, and diols a higher temperature (60 °C) was required. The rates of chromium(V) relative to chromium(VI) oxidations range from 0.08 to over 400.

Introduction

Our recent success in preparing a class of relatively stable water-soluble chromium(V) compounds[2] has opened the way to direct and more systematic investigation of the oxidative properties of chromium(V) in aqueous systems. In this study we are examining the reactions of sodium bis[2-ethyl-2-hydroxybutanoato(2−)]oxochromate(V) (I) with a number of organic compounds and comparing them to the well-known oxidations by chromium(VI).



I

Experimental Section

Materials. Oxalic acid (Fisher), lactic acid (Fisher), 2-oxoglutaric acid (Eastman), 3-oxoglutaric acid (Eastman), 3-phenyllactic acid (Aldrich), glycolic acid (Aldrich), glyoxylic acid (Aldrich), mandelic acid (Aldrich), pyruvic acid (Aldrich), tartaric acid (Aldrich), formaldehyde (Baker, 37% solution), acetaldehyde (Eastman), 1-propanol (Fisher), 2-propanol (Fisher), cyclopentanol (Aldrich), cyclohexanol (Aldrich), ethylene glycol (Fisher), 1,2-propanediol (Aldrich), 2,3-butanediol (Aldrich), pinacol (Aldrich), citric acid (Aldrich), 2-hydroxy-2-methylpropanoic acid (Eastman), 2-hydroxy-2-methylbutanoic acid (Aldrich), and 2-ethyl-2-hydroxybutanoic acid (Aldrich) were used as received. 2-Hydroxy-2-phenylpropanoic acid hemihydrate (Aldrich, 95%) was recrystallized from acetone–hexane and dried in vacuo (30 min at 100 °C) to remove crystalline water. Propanal (Aldrich) and butanal (Aldrich) were freshly distilled. Cyclobutanol (98.5% by GLC) was prepared from cyclopropylcarbinol.[3] Sodium bis[2-ethyl-2-hydroxybutanoato(2−)]oxochromate(V) monohydrate was prepared from sodium dichromate and 2-ethyl-2-hydroxybutanoic acid in acetone.[2] Freshly prepared solutions of chromium(V) were kept in a freezer for no longer than 3–4 days. Solutions of carboxylic acids (0.1 M, 0.5 M) were partially neutralized with sodium hydroxide to achieve the pH 3.0. The pH was verified on a Beckman Expand-Mate pH meter equipped with a Fisher combination electrode. For pH >3 Fisher Cerified buffer solutions were used. Stock solutions of chromium(VI) were prepared from sodium dichromate (Baker Analyzed).

Rate Measurements. At 25 °C chromium(V) and chromium(VI) oxidation rates were measured from decreases in absorbance at 350 nm (ϵ(Cr(V)) = 1209) on a Cary Model 15 recording spectrophotometer equipped with a thermostated cell holder. In a typical run 6–7 μL of a 0.2 M aqueous solution of chromium(V) or 6–7 μL of a 0.1 M solution of sodium dichromate were injected into 2 mL of a 0.1 M solution of the substrate, resulting in a chromium(V) or chromium(VI) concentration of (6–7) × 10^{-4} M. Pseudo-first-order rate constants were determined from plots of log *A* vs. time.

At 60 °C chromium(V) rates were monitored at 750 nm (ϵ = 38, maximum). In a typical experiment 2 mL of a 0.5 M solution of a substrate and 0.01 M of 2-ethyl-2-hydroxybutanoic acid (pH 3.0) were equilibrated for 30 min, and the reaction was initiated by injection of 100 μL of a 0.2 M solution of chromium(V), resulting in a 0.01 M chromium(V) concentration. Chromium(VI) rates were measured at 350 nm (2 mL of 0.5 M substrate, 6 μL of 0.1 M $Na_2Cr_2O_7$; 6 × 10^{-4} M Cr(VI)). Solutions of alcohols, diols, and aldehydes were prepared in hydrochloric acid–potassium phthalate buffer (22.3 mL of 0.1 M HCl + 50 mL of 0.1 M phthalate, pH 3.0).

Product Analysis. The yields of carbon dioxide were determined manometrically at 25 °C in a Warburg apparatus.[4] An aqueous solution of a substrate (3 mL; 0.5 M) was placed into the flask and purged with carbon dioxide for 15 min, and the reaction was initiated by the injection of chromium(V) (50 μL; 0.5 M aqueous solution) by a Hamilton syringe through a side arm fitted with a serum cap. The apparatus was calibrated by the carbon dioxide that was generated by the oxidation of excess oxalic acid under the same conditions.

The yields of formic, acetic, propanoic, and butanoic acids were determined by GLC and those of all other products by HPLC chromatography. Oxidations (0.5 M substrate, 0.05 M Cr(V)) were carried out at 25 or 60 °C with use of sealed reaction ampules (Wheaton Scientific, size 1–2 mL). HPLC analyses were carried out with a Waters Associates Model 6000 A liquid chromatograph equipped with a Model 440 absorbance detector (254 nm) and a C_{18} reverse-phase column. A solvent system was composed of water–methanol–acetic acid (400:100:25, v/v). In GLC analyses 1-mL samples of the reaction mixture were extracted with 1 mL of diethyl ether, chilled in ice, and analyzed on a Fisher-Victoreen Series 4400 gas chromatograph using a 6-ft UC-W98 10% silicon rubber column. The analysis of formic acid was carried out with a TCD detector. Calibration graphs were constructed for each product.

Stability of Chromium(V) Solutions. Solutions of sodium bis[2-ethyl-2-hydroxybutanoato(2−)]oxochromate(V) were prepared in an appropriate amount of perchloric acid or a buffer (Fisher Certified). At 25 °C the disappearance of chromium(V) was monitored at 550 nm (1-cm cell, 2-mL sample; Figure 1). At this wavelength chromium(V) is a dominant absorbing species (ϵ = 105). Absorbances of chromium(VI) (ϵ = 1.5) and chromium(III) (ϵ = 8) are sufficiently low to be negligible in a qualitative study.[5] A 1-h time perid was arbitrarily chosen to allow comparison under different conditions. At the end of the period samples were analyzed by iodometric titration to determine the total content of oxidizing chromium species (chromium(V) and chromium(VI); Table I).

(1) The support of this investigation by a grant of the National Science Foundation is gratefully acknowledged.
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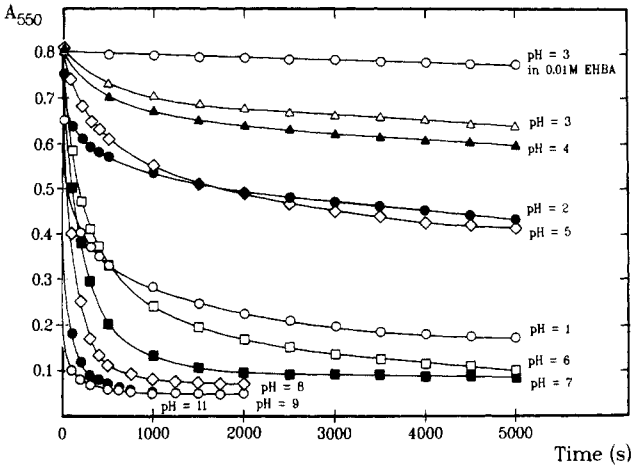

Figure 1. Stability of chromium(V) in aqueous solutions at 25 °C and pH dependence ([Cr(V)] = 7×10^{-4} M, monitored at 550 nm).

Table I. Stability of Chromium(V) in Aqueous Solutions[d]

pH	Cr(V),[a] %	Cr(V) + Cr(VI),[b] %
1.0 (0.1 M $HClO_4$)	22	62
2.0 (0.01 M $HClO_4$)	57	82
3.0 (0.001 M $HClO_4$)	82	87
3.0 (0.01 M EHBA)	96.5	96.5
4.0[c]	80	93
5.0	54	98
6.0	15	100
7.0	0	100
8.0	0	100
10.0	0	100
12.0 (0.001 M NaOH)	0	100
14.0 (0.1 M NaOH)	0	100

[a] Determined spectrophotometrically at 550 nm (Figure 1). [b] Total oxidation power as determined by iodometric titration. [c] For pH 4-10 certified buffer solutions were used. [d] Conditions: [Cr(V)] = 7×10^{-4} M; 25 °C; 1 h.

Results and Discussion

Stability of Chromium(V). Although aqueous solutions of sodium bis[2-ethyl-2-hydroxybutanoato(2−)]oxochromate(V) are unusually stable for a chromium(V) compound, their stability is nevertheless limited. Since the objective of this investigation was to study the oxidation of organic substrates by chromium(V), it was first necessary to determine the range within which chromium(V) solutions would exhibit maximum stability.

The data in Figure 1 and in Table I show decomposition rates of chromium(V) at 25 °C over a wide range of acidities. The stability is strongly acidity dependent; it reaches its maximum within a relatively narrow pH range of 3–4 and is further significantly increased by the addition of a small amount of the free hydroxy acid (2-ethyl-2-hydroxybutanoic acid (EHBA)).

Both the acidity dependence and the stabilizing effect of the free hydroxy acid are consistent with the assumption that the most stable chromium(V) species is I, the monoanion of the chromium(V) complex with two molecules of EHBA, $Cr^{V}O(EHBA)_2^-$, which is in equilibrium with free EHBA in the solution (eq 1 and 2).

$$Cr^{V}O(EHBA)_2^- + H_2O \rightleftharpoons Cr^{V}(EHBA) + EHBA \quad (1)$$

$$Cr^{V}(EHBA) + H_2O \rightleftharpoons Cr^{V}_{aq} + EHBA \quad (2)$$

Lowering the acidity lowers the concentration of EHBA by converting it into the corresponding anion and thus moving both equilibria to the right and producing the much more reactive chromium(V) species $Cr^{V}(EHBA)$ and Cr^{V}_{aq}. For similar reasons the addition of free EHBA has a stabilizing effect by shifting the equilibrium to the left.

The decrease in stability at higher acidities indicates that the neutral chromium(V) EHBA complex $Cr^{V}OH(EHBA)_2$ is less stable than the monoanion $Cr^{V}O(EHBA)_2^-$. This is consistent with our previous observations. While we were successful in preparing a number of fairly stable chromium(V) salts of this type (L in $M^+CrOL_2^-$ is a neutral bidentate ligand),[2] we were unable to isolate any of the free acids.

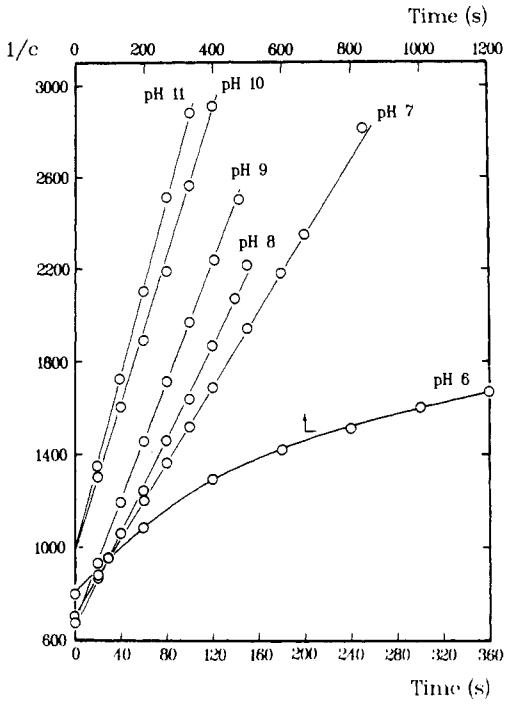

Figure 2. Disproportionation of chromium(V) in the pH range 6–11 (initial [Cr(V)] = 0.0014 M, 25 °C, 500 nm).

Table II. Kinetic Data for the Disproportionation of 0.0014 M Chromium(V) at 25 °C

pH	k, M^{-1} s^{-1}		pH	k, M^{-1} s^{-1}	
7.0	8.2[a]		10.0	15.8[b]	
8.0	10.0[b]	17.5[a]	11.0	19.1[b]	19.0[c]
9.0	13.1[b]	12.9[c]	12.0	>30[d]	

[a] Potassium dihydrogen phosphate–sodium hydroxide buffer. [b] Boric acid–potassium chloride–sodium hydroxide buffer. [c] In the presence of 0.0014 M Cr(VI). [d] In 0.001 M NaOH.

The results in Table I show that at low acidities (pH 6 or higher) chromium(V) undergoes quantitative disproportionation to chromium(VI) and chromium(III) (eq 3).

$$3Cr(V) \rightarrow 2Cr(VI) + Cr(III) \quad (3)$$

The disproportionation reaction is second order in chromium(V) as shown by obtaining good linear plots for $1/c$ vs. time in the pH range 7–11 (Figure 2), and the rate is not influenced by the addition of chromium(VI) (up to 0.0014 M). Therefore, the mechanism of disproportionation can be represented by eq 4 and 5. The values of the second-order rate constants (Table II) depend

$$2Cr(V) \xrightarrow[\text{limiting}]{\text{rate}} Cr(VI) + Cr(IV) \quad (4)$$

$$Cr(V) + Cr(IV) \rightarrow Cr(VI) + Cr(III) \quad (5)$$

not only on the pH but also on the nature of the buffer.

In more acidic solutions the yield of chromium(VI) is significantly reduced (Table I). As Cr(VI) reacts with tertiary hydroxy acids far too slowly to account for the recorded loss in oxidizing power,[4] the lower yield of chromium(VI) must be due to oxidation of the carboxylato ligand within the complex. The higher the acidity, the more successfully ligand oxidation competes with disproportionation.

Chromium(V) Oxidations. The study of chromium(V) oxidations of organic substrates was carried out under conditions in which the chromium(V) complex exhibits maximum stability.

Table III. Kinetic Data for the Oxidation of Carboxylic Acids by Chromium(V) and Chromium(VI) in Water at 25 °C

acid	Cr(V)[a]		Cr(VI)[a]		
	10^4k, s^{-1}	k_{rel}	10^4k, s^{-1}	k_{rel}	$k_{Cr(V)}/k_{Cr(VI)}$
$(COOH)_2$	87	19.3	0.21	0.38	414
$CH_3CH(OH)COOH$	4.5	1.00	0.55	1.00	8.2
$C_6H_5CH_2CH(OH)COOH$	2.5	0.55	1.5	2.7	1.7
$HOCH_2COOH$	0.72	0.16	0.14	0.25	5.1
$HOOC(OH)CHCH(OH)COOH$	115	25.6	5.8	10.5	20
$C_6H_5CH(OH)COOH$	24	5.3	1.4	2.5	17
$C_6H_5(CH_3)C(OH)COOH$	3.8	0.84	0.020	0.036	190
OHCCOOH	10.2	2.3	7.9	14.4	1.3
$CH_3COCOOH$[b]	1.9	0.42	0.040	0.073	48
$HOOCCH_2CH_2COCOOH$[b]	1.2	0.27	0.062	0.11	19
$HOOCCH_2COCH_2COOH$	51	11.3	1.3	2.4	39

[a] Conditions: [Cr(V)] or [Cr(VI)] = 6×10^{-4} M; [S] = 0.1 M; pH 3.0; λ = 350 nm (1-cm cell). [b] λ = 380 nm.

Table IV. Kinetic Data for the Oxidation of Alcohols, Diols, Aldehydes, and Tertiary Hydroxy Acids by Chromium(V) and Chromium(VI) in Water at 60 °C

substrate	Cr(V)[a]		Cr(VI)[b]		
	10^4k, s^{-1}	k_{rel}	10^4k, s^{-1}	k_{rel}	$k_{Cr(V)}/k_{Cr(VI)}$
$CH_3CH_2CH_2OH$	0.45	0.0051	0.032	0.00061	14.1
$(CH_3)_2CHOH$	1.5	0.017	0.051	0.00098	29.4
cyclobutanol	10.1	0.11	0.12	0.0023	84
cyclopentanol	0.47	0.0053	0.090	0.0017	5.2
cyclohexanol	0.20	0.0022	0.075	0.0014	2.7
ethylene glycol	0.17	0.0019	0.16	0.0031	1.06
1,2-propanediol	0.52	0.0058	0.058	0.0011	9.0
2,3-butanediol	1.65	0.018	0.20	0.0038	8.2
pinacol	2.7	0.030	34	0.65	0.079
HCHO	0.38	0.0043	0.34	0.0065	1.1
CH_3CHO	7.1	0.080	0.14	0.0027	51
CH_3CH_2CHO	12.8	0.14	0.32	0.0061	40
$CH_3CH_2CH_2CHO$	18.7	0.21	0.35	0.0067	53
$(CH_3)_2C(OH)COOH$	2.07[c]	0.023	0.55	0.011	3.8
$C_2H_5(CH_3)C(OH)COOH$	0.63[c]	0.0071	0.73	0.014	0.86
$(C_2H_5)_2C(OH)COOH$	0.21[c]	0.0024	0.21	0.0040	1.0
$CH_3CH(OH)COOH$	89[c]	1.00	52	1.00	1.71

[a] Conditions: [Cr(V)] = 0.01 M; [S] = 0.5 M; [EHBA] = 0.01 M; pH 3.0; λ = 750 nm (1-cm cell). [b] Conditions: [Cr(VI)] = 6×10^{-4} M; [S] = 0.5 M; pH 3.0; λ = 350 nm (1-cm cell). [c] No EHBA added.

Oxidation rates of more reactive compounds were measured at 25 °C at pH 3.0 and monitored spectrophotometrically at 350 nm. Under these conditions disproportionation and ligand oxidation were negligibly low in comparison with substrate oxidation.

All compounds readily oxidized at room temperature (Table III) are α-substituted carboxylic acids: hydroxy acids, oxo acids, and oxalic acid. The most reactive among them are tartaric, oxalic, and 3-oxoglutaric acids. The reactivities of other hydroxy and oxo acids lie within a relatively narrow range of values. Lactic acid exhibits a moderate reactivity, and its rate constants are used for comparison. All compounds in Table III show greater reactivity toward chromium(V) than chromium(VI); this is most notable in the case of oxalic and 2-hydroxy-2-phenylpropanoic acids.

The kinetic curves obtained by the oxidation of substrates like oxalic, mandelic, and 2-hydroxy-2-phenylpropanic acids (Figure 3) exhibit a consecutive-type character and consist of two parts: a rapid increase in the absorbance followed by first-order-type decay. Similar changes in the absorbance upon addition of a substrate (usually a hydroxy acid) have been also observed in other regions of the UV–visible spectrum of the chromium(V) complex. This leads us to believe that the oxidation is preceded by a ligand-exchange reaction in which the original 2-ethyl-2-hydroxybutanoato ligand (L) is replaced by one or two substrate molecules (S) (eq 6). The oxidation then occurs within a chromium(V)

$$Cr^VL_2 \underset{-L}{\overset{S}{\rightleftharpoons}} Cr^VLS \underset{-L}{\overset{S}{\rightleftharpoons}} Cr^VS_2 \qquad (6)$$

complex with the reactive ligand (eq 7 or 8) to give chromium(III)

$$Cr^V(EHBA)L \rightarrow Cr(III) + P \qquad (7)$$

$$Cr^VL_2 \rightarrow Cr(III) + P \qquad (8)$$

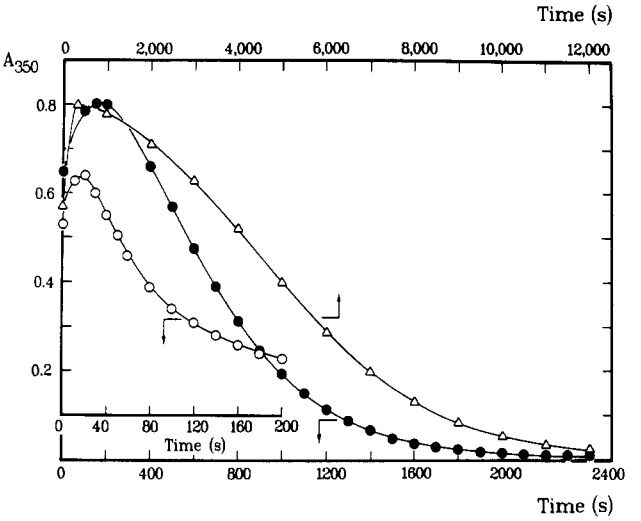

Figure 3. Absorbance (350 nm) vs. time dependence for chromium(V) at 25 °C (initial [Cr(V)] = 5×10^{-4} M, pH 3.0): (○) 0.1 M oxalic acid; (●) 0.1 M mandelic acid; (△) 0.1 M 2-hydroxy-2-phenylpropanoic acid.

and products. From the shape of the curves it is obvious that rates of the ligand-exchange reaction and of the oxidation must be of comparable magnitude.

Most substrates used in this study can undergo oxidation either by carbon–hydrogen cleavage, resulting in the oxidation of a hydroxyl group to a carbonyl group or of an aldehyde group to a carboxyl group, or by carbon–carbon cleavage, leading to the formation of carbon dioxide. From carbon dioxide and other

Table V. Representative Stoichiometric Data for the Oxidation of Carboxylic Acids, Alcohols, Diols, and Aldehydes by Chromium(V) in Water

substrate	3-pentanone,[a] %	CO_2,[b] %	other products,[a] %	substrate	3-pentanone,[a] %	other products,[a] %
$(COOH)_2$[c]	<1	100	...	$C_2H_5(CH_3)C(OH)COOH$[d]	8	92 ($CH_3CH_2COCH_3$)
$HOCH_2COOH$[c]	1	4	96[f] (OHCCOOH)	$(C_2H_5)_2C(OH)COOH$[d]	...	100 ($CH_3CH_2COCH_2CH_3$)
OHCCOOH[c]	<1	98	98 (HCOOH)	$CH_3CH_2CH_2OH$[d]	4	97 (CH_3CH_2CHO)
$CH_3CH(OH)COOH$[c]	<1	4	96[f] ($CH_3COCOOH$)	$(CH_3)_2CHOH$[d]	3	96 ($(CH_3)_2CO$)
$C_6H_5CH(OH)COOH$[c]	<1	93	95 (C_6H_5CHO)	cyclobutanol[d]	2	98 (cyclobutanone)
			5 ($C_6H_5COCOOH$)	pinacol[d]	<1	100 ($(CH_3)_2CO$)
$CH_3COCOOH$[c]	<1	100	99 (CH_3COOH)	CH_3CH_2CHO[d]	3	99 (CH_3CH_2COOH)
$C_6H_5(CH_3)C(OH)COOH$[c,e]	1	100	99 ($C_6H_5COCH_3$)	$CH_3CH_2CH_2CHO$[d]	3	99 ($CH_3CH_2CH_2COOH$)
$(CH_3)_2C(OH)COOH$[d]	9		89 ($(CH_3)_2CO$)			

[a] Conditions: [Cr(V)] = 0.05 M; [S] = 0.5 M. [b] Conditions: [Cr(V)] = 0.01 M; [S] = 0.5 M. [c] 25 °C. [d] 60 °C, CO_2 not determined. [e] [S] = 0.1 M. [f] While these products could be qualitative detected and identified by HPLC, quantitative determination was prevented by complications arising from complex formation with Cr(III). The yield was estimated from CO_2 measurement.

reaction product studies (Table V) it is obvious that carbon–hydrogen bond cleavage is the preferred mode of oxidation in most substrates in which a 2-hydrogen is present. The only exceptions are glyoxylic and mandelic acid; all other 2-hydroxy acids are oxidized predominantly to 2-oxo acids.

Alcohols, diols, aldehydes, and tertiary 2-hydroxy acids generally show considerably lower reactivities (Table IV). Their oxidation rates were therefore measured at 60 °C with use of higher substrate concentrations (0.5 M). As some disproportionation of chromium(V) to chromium(VI) and chromium(III) can occur during the oxidation, these measurements were carried out at 750 nm, where chromium(V) is a dominant absorbing species. Because the absorption of chromium(V) at 750 nm is much lower than at 350 nm (ϵ = 42 vs. 1220), a higher concentration of chromium(V) had to be employed. Rate plots of several typical substrates are shown in Figure 4. Also included is a curve showing log A vs. time for chromium(V) in the absence of a substrate under otherwise identical conditions. From this curve it is apparent that although some decomposition of chromium(V) does take place during the oxidation, it is relatively very low and in most cases can be neglected. Its contribution (<20%) is significant only in the case of the slowest reacting substrates (e.g. ethylene glycol), for which rate constants were obtained by plotting log (A(substrate) − A(Cr(V) dec)) vs. time. As there is no evidence of a preceding ligand-exchange reaction, either the equilibrium concentration of chromium(V) complexes formed from these substrates is too low to be observable or the oxidation proceeds directly, not by way of Cr(V)–substrate complex formation.

Rate constants for chromium(V) oxidations and corresponding chromium(VI) data are given in Table IV. Lactic acid is included to allow comparison with compounds in Table III. Among the compounds whose rates are summarized, aldehydes (except formaldehyde) are among the most reactive. The low reactivity of formaldehyde is surprising and stands in sharp contrast to its normal reactivity toward chromium(VI).[6] Since formaldehyde exists predominantly in the hydrated form,[7] it could indicate that aldehydes react with chromium(V) in their free rather than hydrated form as they do with chromium(VI).[7,8] A rather unexpected result is the unusually high reactivity of cyclobutanol as compared to that of other alcohols.

Chromium(V) shows generally a higher reactivity toward most substrates than does chromium(VI). This is consistent with the general lack of evidence for chromium(V) accumulation during most chromium(VI) oxidations. A notable exception to this rule is pinacol, which is about 12 times more reactive toward chromium(VI) than chromium(V). This may explain why pinacols, together with ethylene glycol (which reacts about equally well with

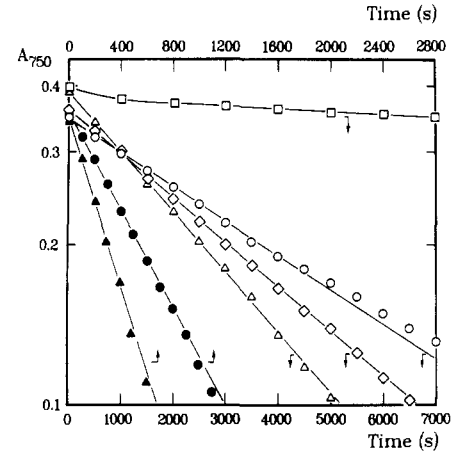

Figure 4. Absorbance (750 nm) vs. time dependence for chromium(V) at 60 °C ([Cr(V)] = [EHBA] = 0.01 M, pH 3.0): (□) no substrate added (stability); (○) 0.5 M 2-propanol; (●) 0.5 M cyclobutanol; (△) 0.5 M pinacol; (▲) 0.5 M butanal; (◇) 0.5 M 2-hydroxy-2-methylpropanoic acid.

Cr(V) and Cr(VI)), have been widely used in the preparation of chromium(V) solution.[9] It should be pointed out that the reaction of pinacol toward chromium(V) is consistent with that of other 1,2-diols; it is pinacol's very high reactivity toward chromium(VI) that is anomalous.[10,11]

Table V gives the quantitative product analysis for most of the substrates in Tables III and IV. Ligand oxidation (leading to 3-pentanone) is generally unimportant (with the exception of tertiary hydroxy acids) even for the least reactive substrates. Most substrates in which either C–H or C–C oxidation could take place give predominantly products of C–H bond oxidation: i.e., alcohols and aldehydes give the corresponding carbonyl compounds and acids, respectively. It is particularly worth noting that cyclobutanol, in spite of its high reactivity, gives the corresponding ketone, cyclobutanone, and not a C–C cleavage product as it does with a number of one-electron oxidants.[12,13] The only compounds that prefer C–C over C–H oxidation (about 20:1) are mandelic and glyoxylic acids.

From the point of view of synthetic applications the results of this study are somewhat disappointing. Although a few compounds (oxalic acid, 2-hydroxy-2-phenylpropanoic acid) show high relative reactivities toward chromium(V) (relative to those toward chro-

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mium(VI)), no general pattern that would make chromium(V) a promising selective oxidant has emerged.

Registry No. I, 70132-29-5; $Na_2Cr_2O_7$, 10588-01-9; HO_2CCO_2H, 144-62-7; $CH_3CH(OH)CO_2H$, 50-21-5; $C_6H_5CH_2CH(OH)CO_2H$, 156-05-8; $HOCH_2CO_2H$, 79-14-1; $HO_2CCH(OH)CH(OH)CO_2H$, 526-83-0; $C_6H_5CH(OH)CO_2H$, 90-64-2; $C_6H_5C(CH_3)(OH)CO_2H$, 515-30-0; $OHCCO_2H$, 298-12-4; $CH_3C(O)CO_2H$, 127-17-3; $HO_2C(CH_2)_2C(O)CO_2H$, 328-50-7; $HO_2CCH_2C(O)CH_2CO_2H$, 542-05-2; PrOH, 71-23-8; *i*-PrOH, 67-63-0; $HO(CH_2)_2OH$, 107-21-1; $CH_3CH(OH)CH_2OH$, 57-55-6; $CH_3CH(OH)CH(OH)CH_3$, 513-85-9; HCHO, 50-00-0; CH_3CHO, 75-07-0; CH_3CH_2CHO, 123-38-6; $CH_3(CH_2)_2CHO$, 123-72-8; $(CH_3)_2C(OH)CO_2H$, 594-61-6; $CH_3CH_2C(CH_3)(OH)CO_2H$, 3739-30-8; $Et_2C(OH)CO_2H$, 3639-21-2; $CH_3CH(OH)CO_2H$, 50-21-5; cyclobutanol, 2919-23-5; cyclopentanol, 96-41-3; cyclohexanol, 108-93-0; pinacol, 76-09-5.

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Hydrogen Isotope Exchange between Boranes and Deuterated Aromatic Hydrocarbons: Evidence for Reversible Hydroboration of Benzene

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Pentaborane(9), B_5H_9, and diborane(6), B_2H_6, undergo hydrogen isotope exchange with deuterated aromatic hydrocarbons. Lewis acid catalyzed hydrogen isotope exchange occurs between benzene-d_6 and the apical hydrogen atom of B_5H_9 to form 1-DB_5H_8 at ambient temperature. In uncatalyzed exchanges, B_5H_9 reacts with deuterated aromatic hydrocarbons to produce 1,2,3,4,5-$D_5B_5H_4$ at +45 °C and B_5D_9 at +120 °C. This thermally induced hydrogen isotope exchange apparently occurs via a reversible hydroboration of the aromatic ring. Diborane undergoes a similar isotope exchange with benzene-d_6 under mild thermal conditions.

Introduction

Hydroboration was discovered in 1936 during a study of the reaction of diborane(6), B_2H_6, with various carbonyl-containing organic molecules.[2] The importance of the reaction grew with the discovery that, on addition of B_2H_6 to asymmetrically substituted olefins, anti-Markovnikov alcohol products were isolated after oxidative workup.[3] Subsequent investigations have established the applicability of hydroboration reductions for carbon–carbon and carbon–heteronuclear multiple bonds of many types. The development of new borane, borane anion, and borane–base adduct reagents has increased the selectivity of the reaction and widened its utility from regiospecific to stereospecific synthetic applications.

Hydroboration reactions involving higher boranes have also been known for many years. The hydroboration of ethylene at elevated temperatures by pentaborane(9), whose structure is shown in Figure 1, was the first reported synthesis of 2-ethylpentaborane (eq 1).[4] Another example is the addition of the 6-SB_9H_{11}

$$B_5H_9 + C_2H_4 \xrightarrow{150\ °C} 2\text{-}EtB_5H_8 \qquad (1)$$

thiaborane to olefins under mild conditions to produce high yields of 9-(alkyl)-6-SB_9H_{11} derivatives.[5] In addition, intramolecular hydroboration has been suggested as a likely mechanism for the rearrangement of 2-(vinyl)B_5H_8 compounds to various derivatives of 2-CB_5H_9.[6]

As a part of our studies of pentaborane rearrangement mechanisms, we have recently explored various methods for labeling B_5H_9 with deuterium. In this paper we report the preparation of deuterium-labeled pentaboranes and diborane by deuterium–hydrogen exchange between the borane and deuterated aromatic hydrocarbons in the presence and absence of $AlCl_3$ catalyst. It appears that this hydrogen–deuterium exchange may be facilitated by reversible hydroboration of the aromatic ring by B_5H_9 and B_2H_6.

Table I. ^{11}B NMR Spectral Data (86.6 MHz)

compd	δ^a (J_{BH}[b]) B(1)	B(2-5)
1-DB_5H_8	−53.4	−13.7 (166)
1,2,3,4,5-$D_5B_5H_4$	−53.4	−13.4
B_5D_9	−53.8	−14.1
B_5H_9	−53.4 (179)	−13.7 (162)

[a] All chemical shifts are referenced against $BF_3{\cdot}OEt_2$. [b] All coupling constants are in Hz.

Results

Lewis Acid Catalyzed Exchange between B_5H_9 and C_6D_6. Deuterium–hydrogen exchange between C_6D_6 and the apical terminal H(1) hydrogen of B_5H_9 occurs in the presence of $AlCl_3$, producing 1-DB_5H_8 at ambient temperature (eq 2). The exchange

$$B_5H_9 + C_6D_6 \xrightarrow{AlCl_3} 1\text{-}DB_5H_8 + C_6D_5H \qquad (2)$$

is typically complete in 1 day. The recovery of the pentaborane is quantitative, and the extent of deuteration of the apical H(1) position is controlled by the C_6D_6:B_5H_9 reactant ratio. ^{11}B NMR data for 1-DB_5H_8 are given in Table I. Insignificant quantities of label are incorporated into the basal terminal H(2–5) positions of B_5H_9 as indicated by the ^1H NMR spectrum and verified by the ^2H NMR spectrum of 1-DB_5H_8 shown in Figure 2. Increasing the reaction temperature to +55 °C does not increase the amount of label in the basal terminal positions. The rate of apical deuteration varies for different pentaborane derivatives, and preliminary results indicate that the rate increases in the order 2-$(Me_3Si)B_5H_8$ < 2-ClB_5H_8 < B_5H_9 < 2-BrB_5H_8. The rate of deuteration at the terminal H(2–5) positions is also affected by substitution on the pentaborane cage. For example, deuterium exchange at the H(4) and H(1) positions in 2-ClB_5H_8 occurs at approximately the same rate.[7]

Thermolysis of B_5H_9 and C_6D_6 or C_7D_8. Deuterium–hydrogen exchange between the terminal H(1–5) hydrogens of B_5H_9 and deuterated aromatic hydrocarbons can be observed at elevated

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