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A Selective Reagent for the Removal and Recovery of Chromate, Molybdate, Tungstate, and Vanadate from Aqueous Solution

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Abstract

4-Aminobenzoic acid, (1-(4-pyridinyl)-2-(1-piperidinyl))ethyl ester, was synthesized and tested to determine its ability to selectively precipitate anions. Fifty-seven common anions were tested. The reagent reacted most readily with the oxyanions of Group VIB and vanadium. The precursor alcohol, 1-(4-pyridinyl)-2-(piperidinyl)ethanol, and the unsubstituted benzoate ester, 1-(4-pyridinyl)-2-(piperidinyl)ethyl benzoate, were also tested. Dissolution of the precipitates in a strong base followed by a methylene chloride wash removes the organic reagent and frees the anions for further analysis.

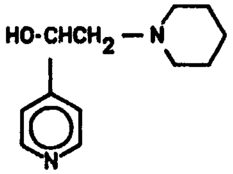
INTRODUCTION

The initial thrust was to prepare a reagent to remove Cr(VI) ions from wastewater and separate Cr(VI) from other ions that might interfere with its determination. Such a reagent has been found and, in addition, it is suitable for the separation of molybdate, tungstate, and vanadate.

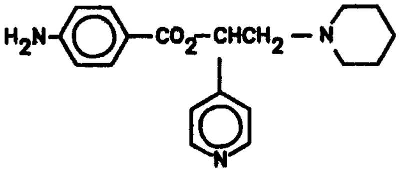
Disposal of hexavalent chromium is regulated by the EPA because of its toxicity. Cr(VI) has been found to be toxic to aquatic life at levels of 20 ppb (*1*) and is classified as carcinogenic and mutagenic (*2*, *3*). In the past, chromate waste was frequently disposed of in lagoons. In some cases the chromate concentration was quite high, and it is believed it migrates from the original sites. Currently, the most widely used method of treatment for chromate-containing waste is reduction, typically with Fe^{2+}, followed by addition of alkali to cause precipitation.

Toxic waste sites can contain a wide variety of compounds, many of which are likely to interfere with analytical measurements. A reagent with high specificity for chromate would be useful in three ways: 1) to more accurately detect chromate, 2) to separate it from many of the interfering substance, and 3) to separate a small group of anions for ordinary analytical purposes.

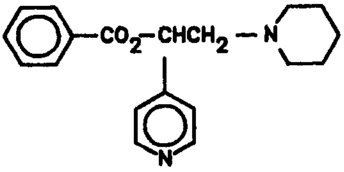
Marvel and Du Vigneaud (*4*, *5*) reported that 4-nitrobenzoic acid, (1-phenyl-2-(diethylamino))ethyl ester, in an acid solution would precipitate nitrate, perchlorate, iodide, oxalate, thiocyanate, and chromate. Chiou et al. (*6*) of our group incorporated this compound into a resin which was selective for nitrate. That work suggested that the phenyl moiety and the amine nitrogen were necessary for reactivity. Models of that polymer indicated that the diethyl groups interfered sterically, and that substitution of a piperidine ring would reduce the problem. Also, if a compound more selective for dianions was desired, substitution of a pyridine ring, with more positive charge capabilities, for the phenyl ring might be helpful. This research describes the behavior of that compound, 4-aminobenzoic acid, (1-(4-pyridinyl)-2-(1-piperidinyl))ethyl ester. Figure 1 shows the structures of three compounds prepared, characterized, and tested.



[1]



[2]



[3]

FIG. 1. Compounds synthesized and tested. [1] 1-(4-Pyridinyl)-2-(piperidinyl)ethanol, [2] 4-aminobenzoic acid, (1-(4-pyridinyl)-2-(1-piperidinyl))ethyl ester, [3] 1-(4-pyridinyl)-2-(piperidinyl)ethyl benzoate.

EXPERIMENTAL

All reagents used in testing were reagent grade and used as received. Solutions were prepared from the following: strontium titanate, selenous acid, metasilicic acid, and orthoperiodic acid; sodium salts of iodate, tungstate, nitroprusside, molybdate, ortho-vanadate, metasilicate, bromate, thiosulfite, dithionite, dichromate, iodide, nitrate, chloride, hydroxide, hydrogen arsenate, sulfate, citrate, oxalate, arsenite, meta-vanadate, selenate, selenite, perchlorate, cyanide, nitrite, fluoride, fluoroborate, hydrogen carbonate, chlorate, hydrogen sulfite, acetate tetraborate, bismuthate, disulfite, borate, periodate, antimonate, orthoperiodate, carbonate, bromide, dithionate, hydrogen sulfate, cyanate, sulfite and sulfide; potassium salts of chromate, permanganate, peroxydisulfate, phosphate, thiocyanate, hexacyanoferrate(II), hexacyanoferrate(III), and dihydrogen phosphate. All water was distilled and deionized.

An Orion pH electrode (#91550) with a LAZAR model DPH digital pH/mV meter was used to determine pH. The synthesized compounds were characterized with a Bruker WM-400 NMR Spectrometer, Finnigan Model 4021 Mass Spectrometer, and Perkin-Elmer Model 283 IR Spectrometer.

Synthetic Procedures

The synthetic schemes used and details of each step were presented by Heininger, as are all spectra (7). All products were spectroscopically characterized. Overall yield of the six-step synthesis of ester [2] was ca. 20%. To determine how the amino group on the phenyl ring influenced the behavior of the reagent, the ester [3] was made without this group.

Analytical Tests

A 0.161-*M* solution of the trihydrochloride salt of [2] was prepared by dissolving 7.0 g in 100 mL water. A solution (0.1 *M*) of each anion was made, and the pH was measured. An anion solution (10 mL) was placed in a test tube, and the reagent solution (2 mL) added. Observations were immediately made on any reactions and again after 2 and 24 hours. In a second set of tests the pH of the anion solution was adjusted to between 5 and 7 when possible (with concentrated solutions of either HCl or NaOH). These neutral solutions were then tested as above. In addition, 0.1 *M* solutions of potassium dichromate or sodium chromate were tested at the following pH's: 1, 3, 6, 8, and 11 (pH adjustments were made with HCl or NaOH).

The same procedure was used to test for precipitates with the dihydrochloride salts of the precursor alcohol, 1-(4-pyridinyl)-2-(piperidinyl)ethanol and (1-(4-pyridinyl)-2-(piperidinyl))ethyl benzoate.

RESULTS AND DISCUSSION

The results of the reactions between each reagent and the anions are summarized in Tables 1, 2, and 3. Fifty-seven anions were tested with the HCl salt of 4-aminobenzoic acid, (1-(4-pyridinyl)-2-(1-piperidinyl))ethyl ester. A more select sample of 33 anions was tested with the salts of the precursor alcohol and the benzoate ester. In general, one of four results was found: no reaction, neutralization of the protonated reagent, precipitation, or some other type of reaction, typically oxidation-reduction. The majority of the anions either did not react or were basic enough to neutralize the reagent and thus cause it to become insoluble in the aqueous solution. It was determined that the material coming out of solution upon the addition of, for example, carbonate was soluble in methylene chloride. The IR and NMR spectra confirmed that the sediment was the free base of the reagent.

Two anions deserve special mention. The permanganate ion formed a large amount of muddy brown sediment, believed to be MnO_2, with each reagent. Nitrite reacted extensively with the aminobenzoate ester with a change in color; however, no reaction occurred with either of the other two compounds. Nitrite is well-known to react with aromatic amines.

No neutralizations are listed as having occurred with the alcohol. This is due to the way this classification was defined. The solubility of the alcohol

TABLE 1
Anion Tests with 1-(4-Pyridinyl)-2-(piperidinyl)ethanol

No Reaction

Chloride
Iodate
Cyanide
Nitrate
Peroxydisulfate
Hydrogen arsenate
Iodide
Perchlorate
Citrate
Tungstate
Oxalate
Nitroprusside
Sulfate
Thiocyanate
Dithionate
Ortho-vanadate
Arsenite
Dichromate (at pH 1)
Nitrite
Phosphate
Dithionite
Bromate
Hydroxide

Reaction

Hexacyanoferrate(II)[a]
Hexacyanoferrate(III)[a]
Permanganate[b]
Molybdate[e]
Chromate[e] (at pH > 3)
Selenite and selenous acid[c]
Selenate[c]
Thiosulfite[d]
Meta-vanadate[e]

[a] Discolored solution slowly.
[b] Due to the loss of color, it is believed that MnO_4^- has been reduced to MnO_2.
[c] Reddish-brown film formed, very fine.
[d] Fine white film formed.
[e] Precipitate formed.

TABLE 2
Anion Tests with 4-Aminobenzoic acid, 1-(4-pyridinyl)-2-(piperidinyl)ethyl ester

No Reaction			
Fluoride	Chloride	Bromide	Iodide
Nitrate	Chlorate	Acetate	Sulfate
Titanate	Selenous acid	Hydrogen sulfite	Dithionite
Dithionate	Hydrogen sulfate	Selenate	Bismuthate
Fluoroborate	Dihydrogen phosphate		
Disulfite	Metasilicic acid		
Neutralization			
Borate	Cyanide	Phosphate	Carbonate
Hydroxide	Citrate	Cyanate	Sulfite
Orthoperiodate	Arsenite	Sulfide	Tetraborate
Hydrogen arsenate	Metasilicate	Hydrogen carbonate	
Reaction but No Precipitate			
Selenite[a]	Thiocyanate[a]	Nitrite[c]	
Perchlorate[a]	Bromate[b]	Orthoperiodic acid[a,b]	
Oxalate[a]	Iodate[b]	Peroxydisulfate[d]	
Thiosulfite[a]	Periodate[b]		
Precipitate Formed			
Chromate	Meta-vanadate		
Tungstate	Nitroprusside		
Antimonate	Molybdate		
Hexacyanoferrate (II) and (III)	Ortho-vanadate		
Dichromate	Permanganate[e]		

[a] Formed a fine film which could not be filtered.

[b] Discolored solution.

[c] Reacted with 1° amine.

[d] Formed a moist, sticky substance which could not be filtered.

[e] Due to the loss of color, it is believed that MnO_4^- has been reduced to MnO_2.

most likely allowed it to remain in solution after deprotonation by highly basic anions.

The precipitates that formed were typically dark, amorphous, and difficult to filter and recover, except those formed with chromate, molybdate, tungstate, and vanadate. The latter three anions are known to form polynuclear species in acidic solutions, and the reagent solution was acidic ($pH < 2$) because the hydrochloride salt of the reagent was used. Thus, it is possible that these anions precipitated due to the formation of these high molecular weight species. However, the supernatant was colorless and

TABLE 3
Anion Tests with Benzoic Acid, 1-(4-Pyridinyl)-2-(piperidinyl)ethyl Ester

	No Reaction		
Chloride	Iodide	Sulfate	Nitrite
Iodate	Perchlorate	Thiocyanate	Selenate
Dithionate	Dithionite	Seleneous acid	Bromate
Nitrate	Peroxydisulfate	Hydrogen sulfite	Oxalate
	Neutralization		
Hydroxide		Ortho-vanadate	
Cyanide		Arsenite	
Chromate (at pH 8 and 11)		Hydrogen arsenate	
Phosphate		Citrate	
	Reaction but No Precipitate[a]		
	Hexacyanoferrate(II) and (III)		
	Precipitate Formed		
Chromate	Dichromate	Molybdate	
Meta-vanadate	Thiosulfite	Nitroprusside	
Permanganate[b]	Selenite[c]	Tungstate	

[a] Discolored solution slowly.
[b] Due to the loss of color, it is believed that MnO_4^- has been reduced to MnO_2.
[c] Precipitate visible after 24 h.

tested negative for reagent. An IR of the dried molybdate precipitate did show a band in the 1700 cm^{-1} region, associated with the carbonyl of the reagent. Some of the anions (e.g., selenite and thiosulfite) formed very fine powderlike films in the test tubes after setting for prolonged periods. Perhaps with more concentrated solutions these anions would form collectable amounts of precipitate. However, the concentration of the tested solutions is already many times more concentrated than natural waters and most industrial effluents, and these anions should not pose a problem with the use of the reagent.

CONCLUSIONS

1. The reagent under investigation, [2], is selective toward a limited number of anions, with the oxyanions of Group VIB and vanadium(V) being foremost among them.

2. The selected anions are, in general, large and either multivalent or easily polarized.
3. The active sites in the molecule are the tertiary amine sites, as suggested by the reactivity of the alcohol.
4. The 1° amine function on the phenyl ring is likely to be a liability in the presence of nitrite.

The following procedure is recommended for the use of the trihydrochloride salt of 4-aminobenzoic acid, (1-(4-pyridinyl)-2-(1-piperidinyl))ethyl ester for removing chromate, molybdate, tungstate, or vanadate from water. Add an aqueous solution of excess organic salt to a neutral or acidic solution containing the ion of interest. Filter the resulting sediments within minutes or, alternatively, decant the supernatant. The addition of NaOH followed by extraction with CH_2Cl_2 (or suitable replacement) will recover the excess reagent. For further analysis of the selected anions, dissolve the collected sediment in a strong base to deprotonate the reagent and free the anions. Extraction with an organic solvent will remove the reagent.

Acknowledgments

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