

Poly(vinylpyridine) Supported Versus Unsupported Ferric Dichromate in Oxidation of Different Organic Compounds

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ABSTRACT

Ferric dichromate and crosslinked polymer of 2- and 4- vinylpyridine supported ferric dichromates are prepared and used effectively as new chromium (VI) reagents for oxidation of different organic compounds such as benzylic and allylic alcohols, aliphatic primary and secondary alcohols, aromatic hydrocarbons, olefinic and acetylinic double bonds, thiols, oximes and ketals. Unsupported ferric dichromate is more efficient. The polymer supported ferric dichromate reagents are milder, easier to handle, more selective, nonhygroscopic, regenerable and environmentally safer to use. These polymeric oxidizing agents are compared with a few other reported polymer supported chromium (VI) reagents.

Key Words

ferric dichromates, polymeric oxidizing agent, polyvinylpyridine supported ferric dichromates, chromium (VI) based oxidants.

INTRODUCTION

There has been a continued interest in the development of new chromium (VI) reagents for the effective oxidation of organic substrates, especially under mild aprotic conditions. For this purpose a number of monomeric chromium (VI) reagents have been reported in the literature [1]. Among these, Jone's reagent [2], Scarett reagent [3], pyridinium dichromate [4], pyridinium chlorochromate [5], nicotinium dichromate [6], quinolinium dichromate [7] and metal dichromate such as zinc dichromate trihydrate [8] and tetrakis (pyridine) silver dichromate [9] can be named.

Polymer supported reagents have found wide application in organic synthesis [10]. Several regenerable polymer supported chromium (VI)

reagents have been reported in the literature. These are polymer - bound chromate based on commercial Amberlyst A-26 resin [11], polyvinylpyridinium chlorochromate [12] and dichromate [13], polyvinylpyridine N-oxide supported dichromates [14] and polyvinylpyridine supported silver dichromates [15]. Use of these polymeric reagents is generally advantageous over their monomeric analogues due to simplification of the reaction work-up i.e. product separation and isolation and their selectivity. In addition, in oxidation reactions, chromium species remain bound to the polymeric support and therefore their toxic environmental effect can be appreciably eliminated.

However, most of the monomeric and, to a lesser extent, polymeric reagents mentioned above suffer from at least one of the following drawbacks: 1) powerful oxidant without selectivity; 2) high acidity of reaction media; 3) use of excess reagent; 4) photosensitivity of the reagent; 5) unstability; 6) hygroscopicity; 7) dangerous procedure for their preparation; 8) tedious work-up; 9) long reaction time; 10) need to use wet reagent; and 11) high cost. Therefore, search for new reagents and methodology is always in demand for synthetic purposes. Along this line, in comparison to the already reported relatively expensive and commercialized tetrakispyridine silver dichromate [9] and its polymeric analogues [15], most recently in a short communication we reported ferric dichromate and linear polyvinylpyridine supported ferric dichromates as less expensive and new oxidizing agents [16]. In this paper we describe fully the preparation and application of ferric dichromate and regenerable crosslinked polyvinylpyridine supported dichromates in oxidation of a variety of organic compounds.

EXPERIMENTAL

Substrates were either prepared in our laboratory or were purchased. Crosslinked porous polymer of 2- and 4- vinylpyridines (2% divinylbenzene), were purchased from Fluka. All oxidation products were known compounds and were identified by comparison of their spectra and physical data with those of the authentic samples. Melting points were determined in open capillaries on Bachi 510 apparatus. The progress of reactions were followed by (GLC), (GC-8A, Carbowax 20 M), or by (TLC) on silica gel polygram SIL G/U.V₂₅₄ plates, and separation of the products was conducted on silica gel columns. Infra-red and nuclear magnetic resonance (¹H 60 MHz) spectra were run on a Perkin Elmer IR 157 G, and Pye Unicams SP9 NMR spectrometer, respectively. The capacity of the reagents were determined by atomic absorption technique and titration method.

Preparation of Ferric Dichromate (FD) [17].

To a solution of CrO₃ (3.36 g, 0.022 mole) in water (50 ml) an excess of freshly prepared ferric hydroxide (prepared from addition of an aqueous solution of NaOH to an aqueous solution of FeCl₃) was added and the resulting mixture, while stirred, refluxed for 4 hours. The reaction mixture was cooled and filtered and the filtrate was evaporated on a rotary evaporator. The resulting deep reddish viscous material was dried in a vacuum desiccator in the presence of P₂O₅ at 40 °C overnight to yield ferric dichromate (90%). It was extremely hygroscopic and care had to be taken when used.

Preparation of Crosslinked Polyvinylpyridine Supported Ferric Dichromates (PVP-FD). To a solution of ferric nitrate nonahydrate (20.2 g, 0.05 mole) in methanol (50 ml), poly 2- or 4- vinylpyridine (2.71 g, 0.025 mole) was added and the mixture stirred for 12 hours at room temperature. The resulting complex was filtered and washed with methanol (2 × 10 ml) and then diethylether (2 × 10 ml). The filter cake was dried in a vacuum desiccator at 50 °C overnight to give P₂VP-Fe(NO₃)₃ (4.6 g) or P₄VP-Fe(NO₃)₃ (4.75 g).

To a cold solution of excess chromium trioxide (15 g, 0.098 mole) in water (15 ml), diluted with acetone (40 ml), (PVP-Fe(NO₃)₃ (4 g) was added and stirred for 1.0 hour, while maintaining the temperature at 5 °C. The resulting mixture was refrigerated overnight and the brown solid was filtered and washed with acetone/water mixture and dried in a vacuum desiccator at 50 °C to give 5.7 g and 5.9 g of P₂VP-FD and P₄VP-FD respectively. The capacities of these reagents were determined to be 2.0 and 2.2 mmole Cr₂O₇²⁻/g of reagents, respectively.

General Procedure for Oxidation of Various Organic Substrates with Ferric Dichromate (FD). Ferric dichromate (0.5-9 mmole) being hygroscopic was quickly weighed and added to a solution of the substrate (1.0 mmole) in acetonitrile (10 ml) and refluxed for 0.3 - 8.5 hours, while stirred. Progress of the reaction was followed by TLC (eluent: CCl₄/ether).

The reaction mixture was then filtered and washed. The combined filtrates were evaporated on a rotary evaporator and the desired compound was

purified by column chromatography using an appropriate eluent. On evaporation of the solvent, the pure products were obtained in 20 to 99% yields. The results are shown in Table 1.

General Procedure for Oxidation of Various Organic Substrates with Polyvinylpyridine Supported Ferric Dichromate (PVP-FD). To a solution of the substrate (1.0 mmole) in the appropriate solvent (12 ml), polymeric reagent, PVP-FD, (0.5-9.0 mmole based on capacities) was added and refluxed while stirred for (1.0-8.0) hours. Progress of the reaction was monitored by TLC or GC. The reaction mixture was cooled to room temperature and filtered followed by repeated washing with the solvent. The combined filtrates were evaporated and the desired compound was obtained and, if necessary, purified by column chromatography using an appropriate eluent. The results are shown in Table 1.

Regeneration of Polyvinylpyridine Supported Ferric Dichromate (PVP-FD). To an aqueous solution of sulfuric acid (2N, 50 ml), the spent reagent (0.3 g) was added and the mixture was warmed and stirred for 1.0 hour. The suspension was filtered and washed successively with a solution of sodium hydroxide (2N) and finally with water. The precipitate was dried in vacuo at 40 °C for 12 hours to give a fine cream colored original polyvinylpyridine which was characterized by its IR spectrum. The ferric dichromate supported reagent made from this polymer sample had the same color and physical appearance as the original reagent, and its activity was the same as that of the fresh reagent.

RESULTS AND DISCUSSION

Ferric dichromate, FD, was easily prepared from chromic acid solution and ferric hydroxide in good yield. It was a stable but extremely hygroscopic compound and care had to be taken for its storage and handling. The acidity of 0.01 molar solution of FD was about 2.19 which is less pronounced than other reported dichromates [16]. It is completely soluble in water and slightly soluble in common organic solvents.

Cross-linked poly (2-vinylpyridine) supported ferric dichromate, XP₂VP-FD, and its 4-isomer, XP₄VP-FD, were synthesized by first preparing the polymer supported ferric nitrate complexes and then exchanging the nitrate with the dichromate anions. The IR spectra of the polymers showed peaks at 765 cm⁻¹ and 930 cm⁻¹, characteristics of dichromate anions [18]. These polymeric reagents were insoluble in almost all organic solvents and were stable and nonhygroscopic compounds. They could be kept for months without any change in their properties. The capacities of these polymeric reagents were determined by both atomic absorption and iodometric titration methods [19]. The values were 2.0 and 2.2 for, XP₂VP-FD, and XP₄VP-FD, respectively, as mmole of Cr₂O₇²⁻ per gram of the reagents.

FD, XP₂VP-FD and XP₄VP-FD, were used efficiently for oxidation of a variety of organic compounds in acetonitrile and methylene chloride as the solvents of choice (Table 1). Where FD, was used, final purification of the products by column chromatography was necessary due to slight solubility of FD and contamination of the final solution with chromium species. In contrast, in the case of the polymeric reagents, chromium anions remained firmly bound to the insoluble polymeric support after the oxidation reactions and therefore product isolation and purification were easily accomplished by filtration of the reaction mixture, evaporation of the solvent and in some cases if necessary further separation of the unreacted starting material or by-products.

As for the reactivities and selectivities of the monomeric versus the polymeric reagents, in general, FD was more reactive and to some extent less selective than the polymeric reagents. As in the case of earlier investigations on polyvinylpyridine supported dichromates [14, 15, 20], it was noticed that, XP₂VP-FD, was more effective than, XP₄VP-FD, in all oxidation reactions. As explained elsewhere, this effect is probably due to a difference in the structures of the two polymer supports [20].

As seen in Table 1, all three reagents oxidized primary and secondary benzylic alcohols

Table 1. Oxidation of different organic substrates with FD (I), XP₂VP-FD (II) and XPVP-FD (III).

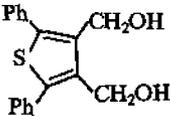
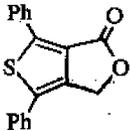
Entry	Substrate	Product	(Oxidant/Substrate) (hrs) (yield)		
			(I) ^a	(II) ^b	(III) ^a
1	Benzylalcohol	Benzaldehyde	(2)(1.5)(75)	(1)(1.5)(80)	(1)(1.5)(35)
2	p-Nitrobenzylalcohol	p-Nitrobenzaldehyde	(4)(7)(99)	(4)(8)(85)	(4)(8)(30)
3	Piperonal	Piperonal	(2)(0.3)(98)	(2)(2)(85)	(2)(2)(20)
4	1-Naphthalenemethanol	1-Naphthaldehyde	(2.5)(2.8)(78)	(2.5)(6)(65)	(2.5)(6)(50)
5	Diphenylcarbinol	Benzophenone	(2.8)(2.6)(95)	(3)(3)(80)	(3)(3)(40)
6	Xanthidrol	Xanthone	(1)(2)(98)	(2)(4)(70)	(2)(4)(65)
7	1-Phenylethanal	Acetophenone	(2.5)(2.6)(89)	(1)(1)(90)	(1)(1)(35)
8	Benzoin	Benzil	(1.8)(1)(89)	(2)(4)(60)	(2)(4)(25)
9	p-Anisoin	p-Anisil	(1)(0.7)(99)	(1)(1.5)(96)	(1)(1.5)(90)
10	Cinnamylalcohol	Cinnamaldehyde benzaldehyde	(2.5)(0.6)(60) (30)	(2)(3)(50)	(2)(3)(10)
11		Monoaldehyde	(3)(1.0)(25)	(2)(6)(trace)	(2)(6)(20)
		Dialdehyde	(32)	(0.0)	(0.0)
			(25)	(90)	(10)
12	1-Heptanol	Heptaldehyde Heptanoic acid	(0.0) (3)(3.5)(88)	(3)(6)(40) (0.0)	(3)(6)(15) (0.0)
13	2-Phenylethanol	2-Phenylacetaldehyde Phenylacetic acid	(7)(4.5)(65) (10)	(3)(5)(55) (0.0)	(3)(5)(15) (0.0)
14	2-Octanol	2-Octanone	(2)(1.5)(85)	(2)(4)(60)	(2)(4)(20)
15	Borneol	camphor	(3)(2.5)(85)	(3)(7)(20)	(3)(7)(10)
16	p-Hydroquinone	p-Benzoquinone	(0.5)(4.0)(86)	(0.5)(3)(60)	(0.5)(3)(20)
17	1,4-Naphthohydroquinone	1,4-Naphthoquinone	(2)(3)(86)	(2)(4)(85)	(2)(4)(80)
18	Anthracene	9,10-Anthraquinone	(4)(3)(98)	(4)(5)(65)	(4)(5)(30)
19	Naphthalene	1,4-Naphthoquinone	(3)(4.5)(60)	no-Rxn	no-Rxn
20	Styrene	Benzaldehyde	(3)(5)(60)	no-Rxn	no-Rxn
21	trans-Stilbene	Benzil	(4)(0.3)(86)	no-Rxn	no-Rxn
22	Diphenylacetylene	Benzil	(9)(8.5)(75)	no-Rxn	no-Rxn
23	Ethylbenzene	Acetophenone	no-Rxn	no-Rxn	no-Rxn
24	Diphenylmethane	Benzophenone	(4)(7.5)(20)	no-Rxn	no-Rxn
25	Thioxanthane	Thioxanthone	(4)(4)(92)	no-Rxn	no-Rxn
26	Thiophenol	Phenyldisulfide	(4.5)(4.5)(40)	(4.5)(7)(95)	(4.5)(7)(90)
27	Pyridinethiol	2-Pyridinedisulfide	(2)(3.5)(83)	(2)(7)(98)	(2)(7.5)(95)
28	Acetophenonoxime	Acetophenone	(2)(2)(80)	(2)(4)(70)	(2)(4)(75)
29	Benzalacetone	Benzalacetone	(2)(2)(73)	(4)(4)(25)	(4)(4)(20)

Table 1. (continued)

30			(1)(0.4)(85)	(1)(5)(70)	(1)(5)(47)
31			(1)(0.4)(80)	(1)(6)(60)	(1)(7)(28)
32			(2)(4)(75)	(2)(7)(65)	(2)(7)(30)

(I), FD = Ferric dichromate.

(II) XP₂VP-FD = Crosslinked poly 2-vinylpyridine supported ferric dichromate.

(III) XP₄VP-FD = Crosslinked poly 4-vinylpyridine supported ferric dichromate.

a: Acetonitrile was used as solvent.

b: Methylenechloride was used as solvent.

to their corresponding aldehydes and ketones without any over-oxidation to the corresponding acid (entry 1-10). An interesting result was obtained in the case of (entry -11). This dialcohol was oxidized by FD to a mixture of the corresponding monoaldehyde, dialdehyde and lactone.

However, when the polymeric reagent, XP₂VP-FD, was used, only lactone was obtained as the major product. Allylic alcohol (entry -10) was oxidized and cleaved by FD, compared to being only oxidized by, XPVP-FD. Overoxidation was noticed in the case of primary aliphatic alcohols when FD was used, but not with the polymeric reagents, (entry 12, 13). Hydroquinones were oxidized to the corresponding quinones in good yield with FD and, XP₂VP-FD, (entry 16, 17). Aromatic hydrocarbons were oxidized to their corresponding quinones with FD, but the polymeric reagents reacted slowly or not at all (entry 18-19). Another interesting behavior of the polymeric reagents compared to FD was that they did not oxidize olefinic or acetylinic linkages, (entry 20-22). Also, in contrast to FD, the

polymeric oxidants did not oxidize the activated benzylic hydrocarbons (entry 23-25). Thiols and oximes were oxidized to their corresponding disulfides and carbonyl compounds in good yield by both monomeric and polymeric reagents (entry 26-29). And finally, deketalization reaction was performed easily by FD and, XP₂VP-FD, in high yields (entry 30-32).

The polymeric reagents, XPVP-FD, could be easily regenerated and used repeatedly with no appreciable loss of activity. Table 2 shows the comparison between these new polymeric reagents and a few other supported chromium (VI) based oxidants reported in the literature for the oxidation of several organic compounds.

In conclusion, although FD is an efficient oxidizing agent for a variety of organic compounds, polyvinylpyridine supported ferric dichromates, XPVP-FD, are milder and more selective, with, XP₂VP-FD, being more efficient. Handling of these polymeric reagents is much easier than handling of FD, and the reaction work-up is not time consuming. No contamination of the environmentally hazardous [21] chromium species

Table 2. Comparison of some polymer supported Cr (VI) based oxidant with, XP₂VP-FD.

Entry	Substrate	Product	(time, hour) (yield %)			
			(XP ₂ VP-FD)	(P ₂ VP-SD) ^a	(PVP-DC) ^b	(P ₂ NO-DC) ^c
1	Benzylalcohol	Benzaldehyde	(1.5)(75)	(0.2)(100)	(18)(99)	(1)(100)
2	1-Phenylethanol	Acetophenone	(2.6)(89)	-d	(24)(99)	(0.75)(95)
3	Cinnamylalcohol	Cinnamaldehyde	(0.6)(60)	(0.6)(100)	(4)(98)	(2)(70)
4	Cyclohexanol	Cyclohexanone	(8)(70)	-d	(68)(66)	-d
5	1-Hexanol	1-Hexanal	(6)(40)	-d	(68)(66)	-d
6	Benzoin	Benzil	(1)(89)	(1.5)(95)	-d	(2.5)(80)

a. P₂VP-SP = poly 2-vinylpyridine supported silver dichromate [15].

b. PVP-DC = polyvinylpyridinium dichromate [13].

c. P₂NO-DC = polyvinylpyridine N-Oxide supported dichromate [14].

d. Data not available.

occurs when the polymeric reagents are used. And finally they can be easily regenerated and reused.

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