

3,5-Dimethylpyrazolium Fluorochromate(VI)-Catalysed Oxidation of Organic Substrates by Hydrogen Peroxide under Solvent-Free Conditions

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Abstract: 3,5-Dimethylpyrazolium fluorochromate (VI), C₅H₈N₂H[CrO₃F], **DmpzHFC**, serves as an efficient catalyst for oxidation of primary, secondary and allylic alcohols to the corresponding carbonyl compounds using H₂O₂ at room temperature under solvent-free conditions. Oxidation of methyl phenyl sulfides and triphenylphosphine were also carried out successfully.

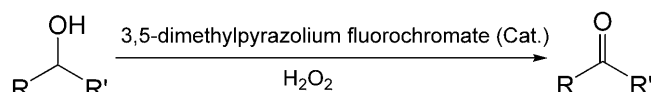
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Over the years, partial oxidation has been one of the fundamental procedures in synthetic organic chemistry. It not only finds application in basic research and pharmaceutical industries but also is regarded as a core technology for converting petroleum-based materials or biomass-based feedstocks to useful chemicals.^[1] Although a wide variety of oxidants, catalysts and reaction systems have been developed, yet, Cr(VI)-based oxidants are extensively used owing to their commendable performance under mild conditions with high efficiency in amounts ranging from stoichiometric to a large excess.^[2–10] Since the chromium residues are environmentally harmful and at times pose difficulties in carrying out the work-up, it would be advantageous to develop Cr(VI)-catalysed oxidation protocols.^[11–13] A large number of catalytic systems has been described using metal complexes associated to peroxo species for alcohol oxidations. Although Cr(VI)-catalysed H₂O₂ oxidations often do not seem to work very efficiently,^[12] our long association with developing Cr(VI) reagents^[7–9] and peroxo-metal chemistries^[14] led us to believe that under appropriately worked out conditions hexavalent chromium would be an effective catalyst for H₂O₂ oxidation of organic substrates. Our perception was further

augmented by the significant contributions of Muzart et al.^[12,13] in the domain of Cr(VI)-catalysed oxidations by TBHP, UHP (urea hydrogen peroxide), SPC (sodium percarbonate) and H₂O₂. The prevalence of controlled acidity of a Cr(VI)(cat)-H₂O₂ system appeared to be one of the most important prerequisites for the success. Based on these factors and also considering the *pK_a* values of **PFC**, **QFC** and **DmpzHFC** being 2.7, 4.7 and 7.8,^[7–9] respectively, it was perceived that **DmpzHFC** should be the preferred catalyst for this purpose.

Since **DmpzHFC** has an inherently controlled acidity (*pK_a* 7.8),^[9] and also since Cr(VI) is capable of activating peroxide through the formation of a variety of peroxo-Cr(VI) species, it was thought to be reasonable to try out the **DmpzHFC**(cat.)-H₂O₂ oxidation of organic substrates, especially alcohols. There have been a number of reasons as to why H₂O₂ was selected as the oxidant of choice. Among TBHP, UHP, SPC and H₂O₂, H₂O₂ is the least costly, most readily available and more importantly a non-waste-producing oxidant. However, H₂O₂ alone does not do the job efficiently, it needs to be activated to utilize its full potentiality.

The present communication reports the results of oxidation of a variety of organic substrates by H₂O₂ under solvent-free conditions using **DmpzHFC** as the catalyst (Scheme 1).



Scheme 1.

Higher valent transition metals react with H₂O₂ quite readily with the formation of a peroxo-metal species although their chemistry is rather complicated. What we learnt from our experience in the field of peroxo-metal chemistry^[14] was that the formation of peroxo intermediates is quite pH dependent and a higher pH gener-

Table 1. DmpzHFC-catalysed oxidation of selected organic substrates using H₂O₂ as oxidant.

Entry	Substrate	Substrate/DmpzHFC/H ₂ O ₂ molar ratio	Time [min]	Product	Yield [%]
1		1:0.01:2	5		81, 18, ^[a] 41 ^[b]
2		1:0.01:2	5		82
3		1:0.01:2	3		82
4		1:0.01:2	2		80
5		1:0.01:2	2		84
6		1:0.01:2	5		87
7		1:0.01:2	30		75
8		1:0.01:2	5		85

^a Reaction with **PFC**(cat.)-H₂O₂.^b Reactions with **QFC**(cat.)-H₂O₂.

ally favours the formation of complexes with a metal: O₂²⁻ ratio of 1: < 1, and that the loss of peroxide is rather controlled with the raise in pH value of the reaction solution.

Accordingly, the oxidations of a selection of primary, secondary and allylic alcohols were carried out with **DmpzHFC**(cat.)-H₂O₂ and the results are summarized in Table 1. The reactions went on quite fast affording the products in very high yield. In fact the conversions appeared to be complete in a few minutes. It is notable that secondary -OH group is chemoselectively oxidized to ketone in the presence of a primary -OH group (entry 4). Allylic alcohols such as cinnamyl alcohol and geraniol (entries 5 and 6) upon treatment with **DmpzHFC**(cat.)-H₂O₂ was converted to the corresponding aldehydes. It may be mentioned that acid-sensitive substrates like geraniol need, in many instances, a buffer in solution-phase oxidations.

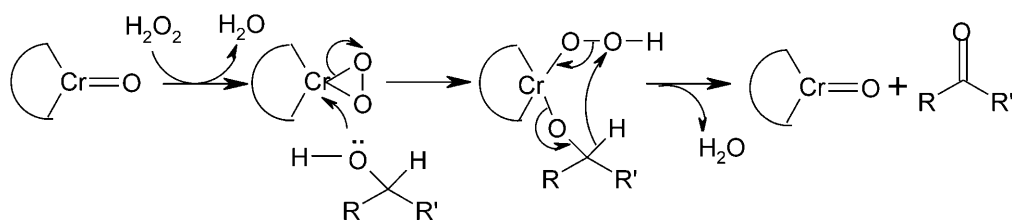
As representative examples of oxo-transfer reactions, **DmpzHFC**(cat.)-H₂O₂ oxidizes methyl phenyl sulfide and triphenylphosphine to methyl phenyl sulfoxide and triphenylphosphine oxide, respectively, (entries 7 and 8).

Importantly, the reactions are very facile, unlike many other cases of Cr(VI)-catalysed aqueous H₂O₂ oxidations.^[12] We did not face any problem with the commercial H₂O₂. The amount of H₂O present in the H₂O₂ solu-

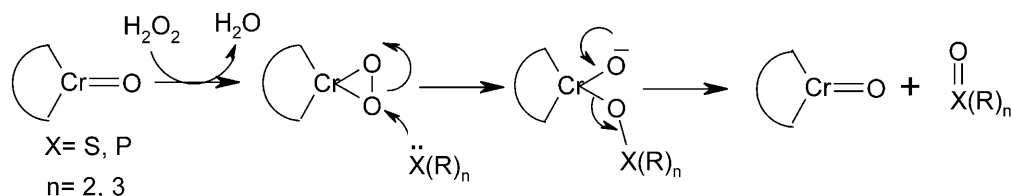
tion did not pose any difficulty. We believe that it is the pH of the reaction solution (*cf.* higher pH), rather than the quantity of water, which is more important.

Similar reactions when conducted with either **PFC** or **QFC** as the catalyst gave very poor yield. For instance, *n*-decanol (entry 1) was reacted with H₂O₂ (2 mmol, 23 μ L) and either PFC (0.01 mmol, 0.0019 g) or QFC (0.01 mmol, 0.0024 g) as catalyst for 5 min to provide the product only in 18% or 41% yield, respectively. Thus the trend is just in the line with the controlled acidity of the chromium catalyst. This supports the view that the lesser the acidity of a Cr(VI)(cat.)-H₂O₂ system the better it is for the oxidation of alcohols, at least within the limits of our experimental conditions. It may be mentioned that on addition of the catalyst, a violet colour was first formed which turned brown as the reactions proceeded. This clearly indicates that H₂O₂ interacts with **DmpzHFC** to form chromium-peroxo complexes *in situ*, which oxidise alcohols to the corresponding carbonyls. Relevantly, the involvement of a peroxo-chromium intermediate was also suggested by Muzart et al.^[12] in their report on alcohol oxidation with TBHP as the oxidant and CrO₃ as the catalyst. The oxidation reaction is likely to proceed *via* the nucleophilic attack by oxygen of alcohols to the metal as depicted in Scheme 2.

The oxo-transfer reaction is expected to progress *via* a metal-oxygen shift mechanism. The ease of formation of



Scheme 2.



Scheme 3.

the sulfoxide or phosphine oxide is likely to happen through the nucleophilic attack by the hetero-atoms (S, P) to the electrophilic O–O bond of a peroxo-metal species thus also facilitating regeneration of the catalyst (Scheme 3).

It may be stated in conclusion that **DmpzHFC** appears to emerge as an appropriate catalyst, for the oxidation of organic substrates, especially alcohols, by H_2O_2 , which is capable of working well with high selectivity. Its inherently controlled acidity seems to be at the hub of its successful performance. This is well supported by the poor performance of its companion catalysts **PFC** and **QFC** having relative higher inherent acidity.

Experimental Section

All procedures were carried out on the bench top. Reagent-grade chemicals were used without further purification. A 30% aqueous solution of H_2O_2 was used for the oxidations. The substrates and solvents were used as received.

The products were characterized by comparing their spectral data recorded on Nicolet Impact – 410 Fourier Transform Infra Red Spectrophotometer and Varian-400 FTNMR. Dime-thylpyrazolium fluorochromate(VI), $\text{C}_5\text{H}_8\text{N}_2\text{H}[\text{CrO}_3\text{F}]$, (**DmpzHFC**), was synthesized by the method described in an earlier communication.^[9]

Oxidation of Organic Substrates by H_2O_2 as the Oxidant and **DmpzHFC** as a Catalyst

First H_2O_2 (2 mmol) and then **DmpzHFC** (0.01 mmol) were added to the substrate (1 mmol) in a mortar. The whole was mixed and left at room temperature with occasional agitation and grinding for the required time given in the Table 1. The progress of the reaction was monitored by TLC. Upon completion of the reaction anhydrous Na_2SO_4 was added to the reaction mixture and then the product was extracted with dichloro-methane (3×15 mL). Evaporation of the organic solvent and

purification by column chromatography afforded the product in good yields (Table 1).

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