

SOME ASPECTS OF PYRIDINIUM FLUOROCHROMATE,  $C_5H_5NHCrO_3F$  (PFC),  
OXIDATIONS. STOICHIOMETRY OF OXIDATION OF ALCOHOLS, EVIDENCE FOR  
OXYGEN TRANSFER, AND THE IDENTITY OF THE REDUCED CHROMIUM  
SPECIES

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Abstract - Molar stoichiometry of the oxidation of *n*-butanol, iso-propanol, benzyl alcohol, or cyclohexanol involving pyridinium fluorochromate,  $C_5H_5NHCrO_3F$  (PFC), in dichloromethane, has been evaluated to be 1:1. The facile oxidation of triphenylphosphine oxide by PFC in acetonitrile provides a clear-cut example of an oxygen transfer reaction. The reduction product of PFC, isolated after such oxidations, has been identified from the results of chemical analyses, chemical determination of the oxidation state of chromium, magnetic susceptibility, ESR and IR spectral studies as  $C_5H_5NHCrO_2F$ , a chromium(IV) species.

Oxidising agents with chromium(VI) as the central atom have always enjoyed a special privilege of a very commonly used oxidant owing to their being versatile, operationally simple, and easily accessible.<sup>2,3</sup> A good amount of work have been accomplished in recent years involving various chromium(VI) species.<sup>4-12</sup> Two such reagents viz., pyridinium chlorochromate,  $C_5H_5NHCrO_3Cl$  (PCC)<sup>6</sup>, and pyridinium fluorochromate,  $C_5H_5NHCrO_3F$  (PFC),<sup>10</sup> have emerged as important additions to the wealth of oxidants. While PCC has already proved itself to be a very powerful oxidant and is used for a variety of oxidations, PFC, with its limited studies so far, has been found to be as reactive as PCC<sup>10,12</sup> with an important additional advantage of its being less acidic<sup>10,12</sup> enabling selective oxidations of alcohols in presence of acid-sensitive compounds without buffering with bases.<sup>12</sup>

We introduced PFC as an oxidising agent first in 1982,<sup>10</sup> and it is incumbent on us to provide some fundamental information concerning PFC oxidations.

In this paper we present the results of studies on stoichiometry of oxidation of alcohols in dichloromethane, oxidation of triphenylphosphine in acetonitrile by PFC, and the nature of reduced product of the oxidant. The results obtained may have relevance in the synthetic operations involving this reagent, and may also be useful in describing a reaction pathway whose essential details may be a common feature in related reactions.

#### EXPERIMENTAL

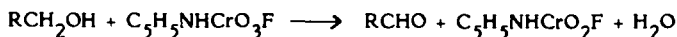
All chemicals were of reagent grade quality. Pyridinium fluorochromate,  $C_5H_5NHCrO_3F$  (PFC), was synthesised and recrystallised by the method described by us.<sup>10</sup> The substrates and the solvents were used after drying and purifying by distillation by usual procedures. The middle fraction were collected after rejecting the head and the tail portions.

The IR spectra were recorded on a Perkin-Elmer model 983 spectrophotometer. Magnetic susceptibility measurements were made by the Gouy method using,  $Hg[Co(NCS)_4]$  as the calibrant. ESR spectra were obtained in the solid state at room temperature on a Varian E-109 ESR spectrometer (X-band) with 100 KHz field modulation.

**Elemental Analyses.** Chromium was estimated iodometrically after oxidizing the compound with acidic persulphate solution. Fluoride content was determined gravimetrically as  $PbClF$ .<sup>13</sup> The per cent composition of carbon, hydrogen and nitrogen were obtained from the Microanalytical Laboratories, RSIC, NEHU, Shillong, and RSIC, CDRI, Lucknow.

**Determination of Stoichiometry. A Typical Procedure.** 10 mmol of *n*-butanol, iso-propanol, benzyl alcohol and cyclohexanol were allowed to react separately with varying amounts (7.5 mmol, 10 mmol, 11 mmol and 12.5 mmol) of PFC in 25 ml of dry dichloromethane under reflux for 2.5-3 hrs in an all

$N_2$  atmosphere. The progress of the reactions were monitored by TLC and analysis of the reaction mixture for corresponding carbonyl compounds was accomplished by the procedure reported in our earlier paper.<sup>10</sup> The percentage conversions to carbonyl compounds were also estimated by preparing their 2,4-dinitrophenyl-hydrazone derivatives. The percent yields of the products with respect to time, in the solvent system, are given in Table, and are consistent with the equation



**Table** Yields of carbonyl products with time in different stoichiometry

Substrate (10 mmol)	Oxidant (mmol)	% Yield of Carbonyl Compounds with Time (min)						
		30	45	60	90	120	150	180
<u>n</u> -Butanol	7.5	25	30	50	60	65	65	-
	10.0	30	38	62	85	94	94	-
	11.0	35	40	65	85	99	99	-
	12.5	35	45	70	85	99	99	-
<u>iso</u> -Propanol	7.5	22	32	45	52	60	64	-
	10.0	30	45	65	80	94	94	-
	11.0	34	50	66	80	98	98	-
	12.5	37	50	70	85	98	98	-
Benzyl Alcohol	7.5	40	50	65	65	65	65	-
	10.0	62	90	93	93	93	93	-
	11.0	65	90	99	99	99	99	-
	12.5	65	90	99	99	99	99	-
Cyclo- hexanol	7.5	15	22	31	40	48	55	60
	10.0	28	35	50	65	75	85	94
	11.0	28	36	50	68	80	90	98
	12.5	30	36	50	70	80	90	98

**Isolation of the Reduced Product,  $C_5H_5NHCrO_2F$ .** In a typical reaction, 15 mmol of the alcohol was allowed to react with 16.5 mmol of PFC in dry dichloromethane under reflux for 2.5 h. A dark product separates out on completion of the reaction. The reaction mixture was cooled to room temperature and the reduced product of PFC was isolated by centrifugation. It was washed repeatedly with dichloromethane and then 2-3 times with ether, when brown microcrystalline  $C_5H_5NHCrO_2F$  was obtained. The compound was finally dried *in vacuo* over phosphorous pentoxide. The yield of  $C_5H_5NHCrO_2F$  was ca 69%.

Anal Calcd. (%) for  $C_5H_5NHCrO_2F$ : C, 32.8; H, 3.3; N, 7.65; Cr, 28.4; F, 10.38. Found: C, 32.6; H, 3.37; N, 7.7; Cr, 28.2; F, 10.5. Estimated oxidation state of Cr: 4.05,  $\mu_{eff}$  at 298 K: 2.91 B.M.

**Reaction of PFC with Triphenylphosphine.** The reaction was performed in all nitrogen atmosphere in a dry 100 ml round bottomed flask and under efficient stirring. To a vigorously stirred solution of 1.5g (5.7 mmol) of triphenylphosphine in 35 ml of acetonitrile, 1.25 g (6.28 mmol) of PFC was added in two instalments in about one minute, maintaining the substrate:oxidant ratio at 1:1.1. An exothermic reaction set in instantaneously, and was complete in 3 min. The solution was cooled and the mother liquor and the washings, after separation of reduced PFC product by centrifugation, was filtered through a short silica gel column (7 cm x 2 cm<sup>2</sup>). The contents of the column were thoroughly washed with ether (3x35cm<sup>3</sup>) and filtered. The combined filtrates were evaporated on a steam bath, and the product was characterised as triphenylphosphine oxide by elemental analyses and IR spectral<sup>14</sup> studies. Yield of OPPh<sub>3</sub>: 1.5 g (94%). M.P.: Found, 155°C (Lit.<sup>15</sup> M.P. 156-157°C).

## RESULTS AND DISCUSSION

It was observed, while carrying out oxidation of alcohols with PFC in dichloromethane,<sup>10</sup> that a brown residue was formed as the reduced product of the oxidant. This was purified by washing with dichloromethane and ether. The product on being treated with acidified KI solution readily liberated iodine causing us to believe that chromium in the reduced product occurs in an intermediate oxidation state, and not chromium(III), and that a three-electron oxidation process is evidently unlikely. Since the oxidations of alcohols to their corresponding carbonyls were complete with the reduction of chromium(VI) to an intermediate oxidation state between +6 and +3, the study of stoichiometry of such a substrate:oxidant was considered important. Accordingly the stoichiometry of oxidations of alcohols viz., n-butanol, iso-propanol, benzyl alcohol, and cyclohexanol involving PFC was evaluated by carrying out reactions separately with each of the afore-mentioned substrates. The molar ratios of the alcohols:PFC were maintained at 1:0.75, 1:1, 1:1.1 and 1:1.25, and it was found that the oxidation in each case was quantitative with the molar

ratio being 1:1.1. While an equimolar amount of PFC did not produce the maximum yield, a molar amount > 1.1 for one mole of the substrate was redundant (Table). The results thus suggest that each of the above oxidations is a two-electron redox process. A slight higher amount of the oxidant than an equimolar amount was required because a very small amount of PFC was found to be entrapped in the mass of the brown reduced product of the oxidant.

Oxo complexes of transition metals are also used as general purpose, stoichiometric oxidants in synthetic organic chemistry,<sup>2,3</sup> and a variety of reaction pathways including both atom-transfer and electron-transfer are involved. In order to get a direct evidence for oxygen transfer, the reaction of triphenylphosphine with PFC (molar ratio of  $\text{PPh}_3:\text{PFC} = 1:1.1$ ) in acetonitrile was carried out at room temperature and triphenylphosphine oxide was obtained in a quantitative yield. This provides a clear-cut example of an oxygen transfer reaction involving PFC, and the result may also be useful in defining other related reactions. The reduction product, here again, was similar to that obtained in the oxidations of alcohols mentioned earlier in this section.

In order to evaluate the consequences of electron-transfer reaction on PFC it was imperative to ascertain the identity of the reduced chromium product. The results of chemical analyses of the brown product revealed the occurrence of  $\text{C}_5\text{H}_5\text{N}:\text{Cr}:\text{F}$  in the atomic ratio of 5:6:1:1, while that of chemical determination of the oxidation state of chromium by iodometry conspicuously showed the presence of chromium(IV). It may be emphasized that the chemical estimation of oxidation state of a metal, capable of displaying variable oxidation numbers, is particularly important and crucial in assessing its actual oxidation state in a specific compound. The room temperature (298 K) magnetic moment of the compound was found to be 2.91 B.M., a value well precedented in the literature<sup>16</sup> for chromium(IV) compounds and is also in agreement with a  $d^2$  configuration of the metal centre. The IR spectra of the compound recorded both in KBr as well as in nujol media showed the characteristics of pyridinium ( $\text{C}_5\text{H}_5\text{NH}^+$ ) ion, and this part of the spectrum is similar to that observed for  $\text{C}_5\text{H}_5\text{NH}^+$  in the case of pyridinium fluorochromate PFC. The additional bands which appeared at 945s, 900s and 645s  $\text{cm}^{-1}$  have been assigned<sup>17</sup> to  $\nu_s(\text{Cr-O})$ ,  $\nu_{\text{as}}(\text{Cr-O})$  and  $\nu(\text{Cr-F})$  modes, respectively, which owe their origins to the presence of coordinated oxo and fluoro groups. Thus, considering the results of elemental analyses, chemically estimated oxidation state of chromium, magnetic susceptibility and IR spectral studies it may be safely inferred that the brown reduced product is  $\text{C}_5\text{H}_5\text{NHCrO}_2\text{F}$  with the metal occurring as chromium(IV).

The compound in its powdered form showed a single band EPR spectrum at 298 K ( $H_0$  at 3312 Gauss) with a g value of  $1.983 \pm 0.005$ . This value is consistent with the presence of a  $d^2$  chromium(IV) species in  $\text{C}_5\text{H}_5\text{NHCrO}_2\text{F}$  and is in agreement with those observed for Cr(IV) compounds at 296-298K by other workers.<sup>18,19</sup> This again lends support to our notion that the chromium of PFC is reduced to a chromium(IV) species in the oxidations of organic substrates studied herein. Further in our endeavour to investigate the behavior of the reduction product of an analogous oxidant pyridinium chlorochromate,  $\text{C}_5\text{H}_5\text{NHCrO}_3\text{Cl}$  (PCC)<sup>6</sup>, the brown reduced product<sup>20,21</sup> was obtained and characterised in manners similar to those described for the PFC reduction product. The compound was identified as  $\text{C}_5\text{H}_5\text{NHCrO}_2\text{Cl}$ . The EPR spectrum of the powdered  $\text{C}_5\text{H}_5\text{NHCrO}_2\text{Cl}$  recorded under analogous conditions showed a pattern similar to that exhibited by  $\text{C}_5\text{H}_5\text{NHCrO}_2\text{F}$  with a g value of  $1.982 \pm 0.005$  rendering us to state that under analogous reaction conditions both PFC and PCC oxidations follow a similar course, and that the fate of chromium in each of oxidations is also similar. These results may also have an implication to synthetic inorganic chemistry in a sense that starting from chromium(VI) compounds an easy access to chromium(IV) compounds may be possible through suitably designed reaction conditions.

#### CONCLUDING REMARKS

The following are the main points emerged out of the present studies:

(1) PFC is an efficient two-electron oxidant, also capable of participating in oxygen transfer oxidations.

(2)  $\text{C}_5\text{H}_5\text{NHCrO}_2\text{F}$  is the reduced product of PFC in two-electron oxidation and oxygen transfer oxidation processes. Similarly, pyridinium chlorochromate,  $\text{C}_5\text{H}_5\text{NHCrO}_3\text{Cl}$  (PCC), is reduced to  $\text{C}_5\text{H}_5\text{NHCrO}_2\text{Cl}$  in analogous reactions. Consequently, it also appears that reduction is suitably chosen chromium(VI) compounds by appropriate organic substrates in an organic medium will provide a very useful

route to the synthesis of, otherwise difficult to obtain, chromium(IV) compounds.

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