Quinolinium Fluorochromate (QFC), $C_9H_7NH[CrO_3F]$: An Improved Cr(VI)-Oxidant for Organic Substrates[1),#]

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Yellow-orange crystalline quinolinium fluorochromate (QFC) is easily prepared in a nearly quantitative yield by the interaction of quinoline with CrO_3 and hydrofluoric acid in 1 : 1.5 : 1 molar ratio. The reagent is stable. Compared with pyridinium fluorochromate (PFC), the new reagent is more soluble in organic solvents and less acidic. QFC in CH_2Cl_2 readily oxidizes primary, secondary, and allylic alcohols to the corresponding carbonyls, benzoin to benzil, and anthracene and phenanthrene to anthraquinone and 9,10-phenanthrenequinone, respectively. Oxidations work well also in a variety of sensitive environments, e.g. isopropylidene functionality and trimethylsilyl ethers. Organic sulfides are transformed to sulfoxides at room temperature. The facile oxidation of triphenylphosphine to triphenylphosphine oxide by QFC in CH_2Cl_2 or CH_3CN provides a clear evidence for an oxygen-transfer reaction. The reduced product of QFC, isolated after such reactions, has been ascertained to be $C_9H_7NH[CrO_2F]$, a chromium(IV) species. The advantages of QFC have been highlighted.

The important prerequisites for an oxidant to be useful are its mildness, versatililty, selectivity, and operational simplicity. Considering these, development of oxidizing agents based upon higher-valent transition-metal oxo derivatives has been the objective of many research laboratories[2)] and a host of such reagents derived from ruthenium, osmium, iron, manganese, molybdenum, chromium, and vanadium have all proven to be capable of alcohol oxidation.[2,3)] Of all such reagents, chromium(VI) oxidants seem to have served organic chemists the most and have undergone a remarkable improvement over the years to suit the needs of practicing chemists. Consequently, pyridinium chlorochromate (PCC),[4,5)] pyridinium dichromate (PDC),[6)] and pyridinium fluorochromate (PFC),[7,8)] have figured as the most significant recent chromium(VI) oxidants.

As part of a program aiming at new reagents and methodologies,[7,9)] PFC–CH_2Cl_2 system was developed in this laboratory,[7)] its efficacy ascertained by us[7)] and others,[8)] and advantages highlighted.[7,8)] Our earlier success and a general perception that nonaqueous conditions are conducive to complex formation of substrates with chromium(VI) species responsible for mild oxidation prompted us to report the results of some highly fruitful experiments involving an improved Cr(VI) reagent, quinolinium fluorochromate (QFC), $C_9H_7NH[CrO_3F]$. The major improvements include the relatively higher solubility of QFC in nonaqueous solvents and its far less pronounced acidic character compared to its companion reagents[7)] PCC and PFC. In addition, the new reagent is as effective as or in some cases even better than PCC and PFC.

Experimental

The chemicals used were of reagent quality. The solvents were first dried and then purified by distillation. The middle fractions were used after rejecting the head and the tail portions.

The IR spectra were recorded on a Perkin–Elmer model 983 spectrometer. ESR spectra were obtained on a solid at ambient temperatures on a Varian E-109 ESR spectrometer (X-band) with 100 KHz field modulation. Magnetic susceptibility measurements were made by the Gouy method using $Hg[Co(NCS)_4]$ as the calibrant. Solution electrical conductance and pH values were measured using a Wayne Kerr automatic Precision Bridge B 905 conductometer and a Systronic type 335 digital pH meter, respectively. Scanning electron micrographs were recorded on JEOL JSM-35CF Scanning Microscope. The NMR spectra were recorded on a 90 MHz Varian EM 390 instrument.

Elemental Analyses. Chromium was estimated iodometrically. In the case of the reduced product of the oxidant, chromium was determined after oxidizing with acidic peroxodisulfate ($K_2S_2O_8$) solution. Fluoride content was determined gravimetrically as PbClF.[10)] The percent composition of carbon, hydrogen and nitrogen were obtained from the Microanalytical Laboratories, Department of Chemistry, NEHU, Shillong.

Synthesis of Quinolinium Fluorochromate, $C_9H_7NH[CrO_3F]$ (QFC). A 30 g (300 mmol) sample of chromium(VI) oxide, CrO_3, and 22.5 cm^3 (450 mmol) of 40% hydrofluoric acid were added to 20 cm^3 of water in a 100 cm^3 polyethylene beaker with stirring. After 5—7 min the homogeneous solution was cooled to ca. 10 °C and 35.5 cm^3 (300 mmol) of distilled quinoline was added, in small portions, to this solution with stirring. This gave yellow-orange crystalline quinolinium fluorochromate (QFC) which was separated by filtration on a polyethylene funnel. It was washed three times with hexane, dried by pressing between folds of a filter paper and finally put under vacuum. The yield of $C_9H_7NH[CrO_3F]$ was 69 g (92.3%). Mp 152—154 °C. Anal. Calcd for $C_9H_8NO_3FCr$: C, 43.38; H, 3.24; N, 5.62; Cr, 20.87; F, 7.62%. Found: C, 43.26; H, 3.35; N, 5.67; Cr, 21.1; F, 7.82%.

The above procedure can be scaled up to larger quantities, if desired. Molar conductances (Λ_M, 25 °C) of 0.001 M solutions (1 M=1 mol dm^{-3}) of QFC in water and in acetonitrile were 138 and 127 Ω^{-1} cm^2 mol^{-1}, respectively. The pH of 0.01 M solution of QFC in water was 3.35.

Oxidation of Organic Substrates with Quinolin-

\# Dedicated to Professor C. N. R. Rao on the occasion of his sixtieth birth anniversary.

ium Fluorochromate (QFC). General Methodology. The oxidations were all conducted in dry apparatus and under efficient stirring. To a thoroughly stirred solution cum suspension of quinolinium fluorochromate (ca. 15 g) in anhydrous dichloromethane (ca. 30 cm^3), the chosen substrate is added in one portion. The molar stoichiometry between the substrate and the oxidant is maintained at $1:1.25$ for alcohols and sulfide, $1:1.1$ for triphenylphosphine, and $1:2.5$ in the cases of trimethylsilyl ether and polycyclic arenes. The reaction mixture is stirred for the time period indicated in Table 1. The oxidations may be conducted under reflux, if desired. The progress of the oxidations may be monitored by TLC on silica-gel using benzene/ethyl acetate (90/10) as the eluent. After the reaction is over, the mixture may be diluted with ether of CH_2Cl_2 and filtered through a short silica-gel column to obtain a clear solution. The solution on evaporation gives the product that may be purified by distillation, recrystallization, sublimation or column chromatography.

Table 1 summarizes the details of the oxidations. The methodology may be scaled up.

Typical Procedures. Oxidation of Citronellol. To a thoroughly stirred suspension cum solution of 2.37 g (9.5 mmol) of quinolinium fluorochromate (QFC) in 5 cm^3 of anhydrous dichloromethane was added 1.18 g (7.6 mmol) of citronellol in 5 cm^3 of CH_2Cl_2 in one portion. The reaction was worked up after 50 min as described above. This afforded a crude product which on being purified by column chromatography on silica-gel gave 1.0 g (85.5%) pure citronellal. Mp, IR and NMR spectra of the compound were identical with an authentic material.

Reaction of QFC with Triphenylphosphine. The oxidation reaction was conducted under nitrogen atmosphere. In a 100 cm^3 round-bottom flask was placed 2.09 g (8.39 mmol) of QFC and 4 cm^3 of anhydrous CH_2Cl_2. Triphenylphosphine (2.0 g, 7.63 mmol) dissolved in 3 cm^3 of CH_2Cl_2 was added in one portion maintaining the substrate : oxidant mol ratio of $1:1.1$. An instantaneous exothermic reaction set in and the oxidation was complete in 2—3 min. The reaction solution was separated by centrifugation and then filtered through a short (7 cm×2 cm^2) silica-gel column. The column material was washed thoroughly with ether and filtered. The combined filtrates and washings were evaporated on a steam-bath and the white highly crystalline product thus obtained was ascertained by chemical analysis, mp, IR and NMR experiments to be triphenylphosphine oxide. Yield of $OPPh_3$: 2.02 g (95%).

Isolation of the Reduced Product, $C_9H_7NH[CrO_2F]$. In a representative procedure, 12 mmol of an alcohol selected from Table 1 or triphenylphosphine was reacted with 13.2 mmol of QFC in anhydrous CH_2Cl_2 under reflux for ca. 1 h to ensure complete reduction of QFC. The reaction mixture was cooled to room temperature and the reduced product of QFC isolated by centrifugation, washed three times with ether and finally dried in vacuo. over P_4O_{10}. The yield of $C_9H_7NH[CrO_2F]$ was 92%. Anal. Calcd for $C_9H_8NO_2FCr$: C, 46.35; H, 3.47; N, 6.01; Cr, 22.30; F, 8.15%. Found: C, 46.12; H, 3.71; N, 6.16; Cr, 22.1; F, 8.23%. Chemically determined oxidation state of Cr: 3.9—4.1. μ_{eff}/BM at 298 K: 2.92.

Determination of pK_a Values. The pK_a values of PCC, PFC, and QFC have been determined considering an equilibrium of the type $AHCrO_3X \rightleftharpoons H^+ + [ACrO_3X]^-$, wherein A refers to pyridine or quinoline and X represents Cl or F. The acid dissociation constant K_a of the compounds can be written as:

$$K_a = \frac{\alpha^2 c}{(1-\alpha)}, \tag{1}$$

where α is the degree of dissociation and c is the concentration of the solution. Accordingly, the term αc corresponds to the equilibrium concentration of H^+ or $[ACrO_3X]^-$. Since H^+ ion concentration is obtained from the experimentally measured pH value of the solution, the degree of dissociation, α, can be determined from the following relation:

$$\alpha = 10^{-\mathrm{pH}}/c \tag{2}$$

The K_a value is then obtained by substituting the value of α in Eq. 1. This is finally converted into pK_a (through p$K_a = -\log K_a$). The pK_a values of PCC, PFC, and QFC thus determined are 1.4, 2.7, and 4.7, respectively.

Results and Discussion

The Reagent (QFC) and Its Characteristic Features. The reagent quinolinium fluorochromate, $C_9H_7NH[CrO_3F]$ (QFC), is easily prepared from the direct interaction of CrO_3 with HF and quinoline in an aqueous medium. QFC is obtained in quantity as yellow-orange small crystals. The scanning Electron Micrograph (SEM) of the product (Fig. 1) evidences for its homogeneity and rod shaped external crystal morphology. It melts sharp at 152—154 °C and is stable over several months. It does not appear to be hygroscopic. The compound is diamagnetic and EPR silent with the chemically estimated oxidation level of chromium being six. The compound analyzed excellent and its solution electrical conductance (Λ_M in H_2O and CH_3CN being 138 and 127 $\Omega^{-1}\,cm^2\,mol^{-1}$, respectively) was in conformity to the formula. $C_9H_7NH^+[FCrO_3]^-$. The characteristic IR spectrum of QFC include bands at 1053, 949, 611, 379, 342, and 272 cm^{-1} attributable[11,12] to $\nu_4(Cr–O_{asym})$, $\nu_1(Cr–O_{sym})$, $\nu_2(Cr–F_{str})$, $\nu_5(O–Cr–O)$,

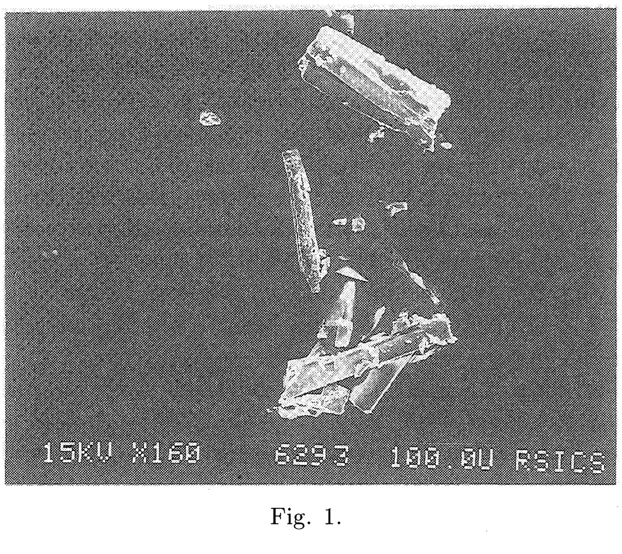
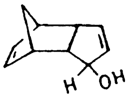
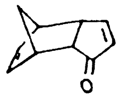
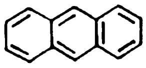
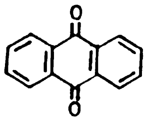
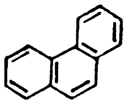
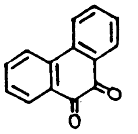
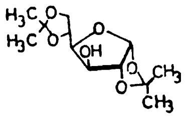
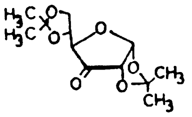
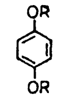
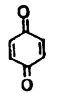


Fig. 1.

Table 1. Oxidation of Alcohols, Polycyclic Arenes, Triphenylphosphine, Trimethylsilyl Ether, and Diphenyl Sulfide with Quinolinium Fluorochromate

Entry	Substrate	Solvent	Reaction time	Product[a)]	Yield(%)
1	1-Butanol	CH_2Cl_2	1.5 h	Butanal	95
2	Benzyl alcohol	CH_2Cl_2	30 min	Benzaldehyde	94
3	Citronellol	CH_2Cl_2	50 min	Citronellal	85.5
4	Isopropanol	CH_2Cl_2	1 h	Acetone	93
5	Cyclohexanol	CH_2Cl_2	1.5 h	Cyclohexanone	93
6		CH_2Cl_2	1 h		94
7	Benzoin	CH_2Cl_2	2 h	Benzil	98
8		CH_2Cl_2 AcOH	3.5 h 30 min		72 96
9		CH_2Cl_2 AcOH	4 h 1 h		60 94
10	Triphenylphosphine	CH_2Cl_2 CH_3CN	3 min 3 min	Triphenylphosphine oxide	95 94
11		CH_2Cl_2	1.5 h		86
12	 R=Si(CH_3)$_3$	CH_2Cl_2	1 h		98
13	Diphenyl sulfide	CH_2Cl_2	13 h	Diphenyl sulfoxide	82

a) Products were characterized by comparison with authentic samples (NMR and IR spectra, thin layer chromatography, GLC analysis and mp/bp measurements).

ν_3(O–Cr–O+O–Cr–F), and ν_6(O–Cr–F), respectively. The vibrational spectrum is typical of fluorochromate(VI), $[CrO_3F]^-$, ion.[7,11,12]

Most significant are the far less acidic character of QFC and its enhanced solubility in organic solvents. The pH values of 0.01 M aqueous solutions of PCC,[7] PFC,[7] and QFC are 1.75, 2.45, 3.35, respectively, showing that QFC is the least acidic of the three reagents. An enhanced hydrogen bonding is, we believe, responsible for this character of the reagent. The relative acidities of the three reagents can be contrasted in a quantitative way in terms of their pK_a values. The experimentally determined pK_a values in going across the series PCC, PFC, and QFC are 1.4, 2.7, and 4.7, respectively (vide Experimental). The solubility properties of QFC is very favorable to an oxidant. While in water it is far less soluble than PCC and PFC, in organic solvents like dichloromethane, acetonitrile, carbon tetrachloride, chloroform the new reagent is relatively more soluble than the other Cr(VI) reagents. In addition quinolinium fluorochromate is soluble also in DMF, THF, and acetone.

Applications of QFC to Oxidations of Organic Substrates. Quinolinium fluorochromate, $C_9H_7NH[CrO_3F]$ (QFC), is an efficient reagent capable of oxidizing a wide variety of organic substrates. As summarized in Table 1, quinolinium fluorochromate–CH_2Cl_2 system readily oxidizes primary (**1**, **2**, **3**), secondary (**4**, **5**), and allylic (**6**) alcohols exclusively to the corresponding carbonyls in practically quantitative yields. Notable in this context is the oxidation of citronellol (**3**) to citronellal without the use of a buffer. This exemplifies a distinctive advantage of QFC over its companion reagents (cf. PCC[4,5] and PFC[7,8]). This result is believed to be a direct consequence of the far less pronounced acidic character of the new reagent.

To enable a direct comparison of the efficiency of QFC with that of an acknowledged efficient oxidant PFC,[7] the chosen substrates in the present investigation have been kept largely similar to those used earlier for PFC oxidations.[7]

Apart from the oxidation of alcohols, the use of QFC as an oxidant for hydrocarbons is very promising. QFC in anhydrous CH_2Cl_2 oxidizes fused-ring hydrocarbons like anthracene and phenanthrene to anthraquinone and 9,10-phenanthrenequinone with the yields of the product being ca. 72 and ca. 60%, respectively. Notable is that these yields are the highest, to the best of our knowledge, achieved under mild conditions. The conversions can be bettered (>90%) by the use of acetic acid in place of CH_2Cl_2. Oxidations work also very well in sensitive environments. Thus the facile oxidations of a secondary hydroxyl group in an environment of isopropylidene functionality (**11**) and a bis(trimethylsilyl ether) (**12**) to the corresponding ketone (86%) and quinone (98%), respectively, at room temperature support the contention. In addition, the reagent oxidizes organic sulfides. Typically diphenyl sulfide (**13**) is oxidized quantitatively to diphenyl sulfoxide at room temperature. Under the present experimental conditions, formation of sulfone was not observed and the relative rate of sulfide oxidation was found to be faster with QFC than PFC.

Furthermore, the new reagent (QFC) also proves to be a very effective oxo-transfer agent. Thus, a stoichiometric reaction between triphenylphosphine (PPh_3) and the reagent (1:1.1 mol ratio) at ambient temperatures in CH_2Cl_2 or CH_3CN solvent afforded triphenylphosphine oxide in a quantitative yield. This gives a clean example of an oxygen-atom-transfer reaction and may have a direct implication in understanding the course of the related reactions.

With the efficacy of quinolinium fluorochromate, $C_9H_7NH[CrO_3F]$, being very convincing, it became imperative to ascertain the identity of the reduced chromium product. This is important for it provides a clear-cut evidence for the number of electrons involved in an electron-transfer reaction. The knowledge is important in understanding the course of such processes. The reduced chromium products isolated after working up the alcohols oxidation as well as PPh_3 oxidation reactions were similar. The brown microcrystalline insoluble product analyzed for $C_9H_7NH[CrO_2F]$ and the iodometrically determined oxidation level of Cr was +4. The compound was paramagnetic with the magnetic moment being 2.92 μ_{BM}/Cr (297 K), while its powder EPR (297 K, H_0 at 3312 Gauss) spectrum exhibited a single band at a g value of 1.982 ± 0.005. These values are very characteristic for the occurrence of Cr(IV)[7,13,15] in the compound. Consistent with the formula of the product, the ν_{sym} (Cr–O), ν_{asym} (Cr–O), and ν (Cr–F) have been observed at 950s, 890m, 620m cm^{-1}, respectively, in its IR spectrum. Thus a combination of chemical analyzes, chemical determination of oxidation state of the metal, IR, magnetic susceptibility, and EPR measurements conclusively supports the formulation of the product as $C_9H_7NH[CrO_2F]$ containing Cr(IV). The result shows inter alia that the reagent acted as a two-electron oxidant in each of the reactions included herein.

Concluding Remarks

This study complements previous work in this laboratory on the development of newer oxidant systems[7,9] for a variety of organic substrates. The easily preparable and stable new reagent quinolinium fluorochromate (QFC), $C_9H_7NH[CrO_3F]$, is comparatively more soluble in organic solvents and far less acidic than the companion reagents[7] PCC and PFC . The QFC–CH_2Cl_2 oxidation methodology is applicable to a wide variety of compounds and provides scopes for newer oxidations. The reagent appears to be suitable also for the oxidation of acid sensitive substrates without the use of a buffer. An important implication of $C_9H_7NH[CrO_2F]$ (a Cr(IV) species) being the reduced product of QFC is that the reagent is certainly a two-electron oxidant system.

Based upon the results obtained so far, QFC appears to be a very useful oxidant also capable of participating in O-atom-transfer reactions and thus it is yet another valuable addition to the domain of the existing oxidants.

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References

1) A preliminary account of our results on the reactivity of this reagent (QFC) was reported: "13th International Symposium on Fluorine Chemistry," Ruhr University, Bochum (FRG), September 1—6, 1991.

2) W. J. Mijs and C. R. H. I. De Jonge, "Organic Syntheses by Oxidation with Metal Compounds," Plenum Press, New York (1986).

3) D. G. Lee and T. Chen, *J. Org. Chem.*, **56**, 5341 (1991), and references cited therein.

4) E. J. Corey and J. W. Suggs, *Tetrahedron Lett.*, **1975**, 2647.

5) G. Piancatelli, A. Scettri, and M. D'Auria, *Synthesis*, **1982**, 245.

6) E. J. Corey and G. Schmidt, *Tetrahedron Lett.*, **1979**, 399.

7) M. N. Bhattacharjee, M. K. Chaudhuri, H. S. Dasgupta, N. Roy, and D. T. Khathing, *Synthesis*, **1982**, 588; M. N. Bhattacharjee, M. K. Chaudhuri, and S. Purkayastha, *Tetrahedron*, **43**, 5389 (1987); M. N. Bhattacharjee, M. K. Chaudhuri, *Inorg. Synth.*, **27**, 310 (1990).

8) T. Nonaka, S. Kanemoto, K. Oshima, and H. Nozaki, *Bull. Chem. Soc. Jpn.*, **57**, 2019 (1984); K. K. Banerji, *J. Chem. Soc., Perkin Trans. 2*, **1988**, 547; *J. Org. Chem.*, **53**, 2154 (1988); S. Agarwal, K. Chowdhury, and K. K. Banerji, *J. Org. Chem.*, **56**, 5111 (1991); A. Moondra, A. Mathur, and K. K. Banerji, *J. Chem. Soc., Dalton Trans.*, **1990**, 2697.

9) M. Bhattacharjee, M. K. Chaudhuri, S. K. Chettri, N. S. Islam, and S. Roy Barman, *J. Mol. Catal.*, **78**, 143 (1993).

10) A. I. Vogel, "A Text Book of Quantitative Inorganic Analysis," Longmans, Green and Co., New York (1962), p. 295.

11) R. Colton and J. H. Canterford, "Halides of the First Row Transition Metals," John Wiley & Sons, New York (1969), p. 190.

12) M. K. Chaudhuri, H. S. Dasgupta, and N. Roy, *Indian J. Chem.*, *Sect. A*, **20**, 1227 (1981).

13) M. Hagihara and M. Yamasaki, *J. Am. Chem. Soc.*, **81**, 3160 (1959).

14) W. Mowat, A. Shortland, G. Yagupsky, N. J. Hill, M. Yagupsky, and G. Wilkinson, *J. Chem. Soc.*, *Dalton Trans.*, **1972**, 533.

15) G. A. Ward, W. Kruss, B. K. Bower, and J. C. W. Chein, *J. Organomet. Chem.*, **42**, C43 (1972).