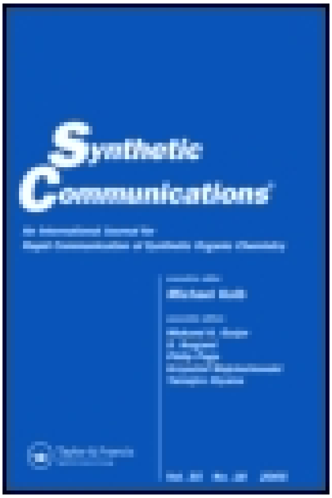

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Synthesis of Halochromates with Inorganic Stable Complex Cations: New, Mild and Efficient Oxidants

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Synthesis of Halochromates with Inorganic Stable Complex Cations: New, Mild and Efficient Oxidants

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Abstract

The halochromates of general formulas of $[M(en)_3][XCrO_3]_3$ (X=Cl,F ; M=Co,Cr) and $[Co(NH_3)_6][XCrO_3]_3$ (X=Cl,F) were prepared and characterized by IR spectroscopy and elemental analysis. These oxidants were examined for oxidizing some alcohols to their aldehydes and ketones and their oxidizing ability was compared with other relevant oxidants.

The chromium (VI) compounds, including chromates, dichromates and halochromates(CrO_3X^- , X = F , Cl , Br , I) are considered amoung the strong and efficient oxidants, that can oxidize almost all the functional group of organic compounds in acidic aqueous conditions.(1-5) Since most of the organic compounds are insoluble in water and sensitive to acidic solutions, synthesis of oxidants based on chromium(VI) for oxidizing functional in mild and non-aqueous media is of a great importance. One of the methods used for preparing such oxidants, is the exchange of their cation with large organic or other metalic cations.(4-8) By this way, pyridinium chlorochromate (PCC)[9,16] , pyridinium fluorochromate (PFC)[10], zinc chlorochromate[6], trimethylammonium chlorochromate (TMACC)[12], pyrazinium chlorochromate[11,13], quinolinium

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fluorochromate(QFC)[14] and 4-dimethylaminopyridinium chlorochromate[15],have been prepared.

On the bases of the stability of some inorganic complex cations such as $[Co(en)_3]^{3+}$, $[Cr(en)_3]^{3+}$ and $[Co(NH_3)_6]^{3+}$, we have used these complexes to prepare six new oxidants based on chromium (VI). Since these oxidants are rather insoluble in many organic solvents and have large cations, they show much milder oxidizing power than other similar oxidants. They are also rather stable and can oxidize alcohols to their aldehydes or ketones in dried dichloromethane or acetone. The yield of the oxidation reaction of alcohols with these oxidants were compared with other oxidants , such as, pyridinium chlorochromate (PCC) and pyridinium fluorochromate (PFC).(table 1)

Experimental

All the reagents were provided from Fluka or Merck and used as recieved.$[Co(en)_3]Cl_3$, $[Co(NH_3)_6]Cl_3$, $[Cr(en)_3]Cl_3$, $KClCrO_3$, $KFCrO_3$, $[Co(en)_3]F_3$, $[Cr(en)_3]F_3$ and $[Co(NH_3)_6]F_3$ were prepared by the methods mention in references (17-22).

Preparation of tris(ethylenediamine)cobalt(III) chlorochromate(1) , tris(ethylenediamine)chromium(III) chlorochromate(2) and hexaminecobalt(III) chlorochromate(3).

To a solution of 1N HCl (40mL), $[Co(en)_3]Cl_3$(3.46g , 0.01mol) was added with stirring at 0°C. To this solution $KClCrO_3$ (5.24g , 0.03mol) was slowly added over a period of 15 min and stirred for 10 min after the addition. The precipitated orange solid was isolated by filtration, washed with CH_2Cl_2 and dried in vacuum oven. Yield: 5.12g (80%).

$C_6H_{24}Cl_3CoCr_3N_6O_9$ (645.6) (1)

Anal: Found: Co 9.00% ; Cr 24.45% , Calc.: Co 9.13% ;Cr 24.16%

IR (KBr): ν=3495,3205,2900,1549,1152,1053,949,909,775,439 cm^{-1}

Complexes (2) and (3) can be also prepared by this method and the obtained yields were (75%) and (70%) respectively.

$C_6H_{24}Cl_3Cr_4N_6O_9$ (638.6) (2)

Anal : Found : Cr 32.38% , Calc.: Cr 32.57%

Table (1): Oxidation of some alcohols with halochromate complexes and compared with pyridinium chlorochromate(PCC) and pyridinium fluorochromate (PFC).

		Halochromate complexes								(PCC)[9,16]			(PFC)[10]		
Substrate	Product	Reaction	Oxid.	Yield(%)						Reaction	Oxid.	Yield(%)	Reaction	Oxid.	Yield(%)
		Time(h)	React.	1	2	3	4	5	6	Time(h)	React.		Time(h)	React.	
PhCH$_2$OH†	PhCHO	2	1.5	78	76	75	85	86	84	5min	0.75	84	45min	1.25	90
phCH$_2$OH††	PhCHO	2	1.5	85	87	81	90	92	90	-	-	-	-	-	-
Cyclohexanol†	Cyclohexanone	3.5	2	72	74	70	83	83	80	-	-	-	3.5	1.5	89
Cyclohexanol††	Cyclohexanone	3.5	2	81	82	80	92	89	90	-	-	-	-	-	-
n - C$_4$H$_9$ - OH†	C$_4$H$_8$O	3	2	71	70	68	80	81	79	-	-	-	2	1.5	94
n - C$_4$H$_9$ - OH††	C$_4$H$_8$O	3	2	85	83	80	91	90	92	-	-	-	-	-	-
Catechol†	o-Benzoquinone	15 nin	1	95	96	95	100	100	100	-	-	-	-	-	-
1 - Heptanol†	C$_7$H$_{14}$O	2	1.5	74	72	75	80	81	83	1.5	1.5	78	1	1.5	84
1 - Heptanol††	C$_7$H$_{14}$O	1.5	1.5	75	73	77	84	87	90	-	-	-	-	-	-

†: Reaction in methylene chloride.
††: Reaction in acetone.

IR (KBr): ν=3505,3205,2900,1535,1145,1049,946,910,773,434 cm^{-1}

$H_{18}Cl_3CoCr_3N_6O_9$ (567.4) (3)

Anal : Found : Co 10.48% ; Cr 27.12% , Calc.: Co 10.39% ; Cr 27.46%

IR (KBr): ν=3450,3280,3135,1598,1332,945,908,844,433 cm^{-1}

Preparation of tris(ethylenediamine)cobalt(III) fluorochromate(4) , tris(ethylenediamine)chromium(III)fluorochromate(5) andhexaminecobalt(III) fluorochromate(6).

Chromium (VI) oxid, CrO_3(3.3g , 0.033mol) was dissolved in hydrofluoric acid (15mL) in a polythene beaker at 0°C. After 5 min of stirring, a clear orange solution is obtained. To this solution $[Co(en)_3]F_3$ (2.96g , 0.01mol)was added slowly with stirring in several portions. Stirring was continued for 15 min after the addition. The mixture was allowed to stand for 10 min. The precipitated orange solid was isolated by filtration and washed with acetone and dried in vacuum oven. Yield: 5.1g (85%).

$C_6H_{24}F_3CoCr_3N_6O_9$ (596.2) (4)

Anal : Found : Co 10.13% ; Cr 26.00% , Calc.: Co 9.88% ; Cr 26.16%

IR (KBr):ν=3500,3195,2960,1548,1158,1056,949,915,775,636 cm^{-1}

Two complexes (5,6) were made by the same procedure discussed in method. The yield of complexes (5) and (6) were 78% , 80% respectively.

$C_6H_{24}F_3Cr_4N_6O_9$ (589.3) (5)

Anal : Found : Cr 35.2% , Calc.: Cr 35.3%

IR (KBr): ν= 3505,3215,2970,1557,1145,1052,952,908,772,638 cm^{-1}

$H_{18}F_3CoCr_3N_6O_9$ (518.0) (6)

Anal:Found : Co 11.26%; Cr 29.35%, Calc.: Co 11.37% ; Cr 30.11%

IR (KBr) : ν=3450,3275,1606,1338,952,913,838,639 cm^{-1}

Oxidation of benzyl alcohol by complex (1)

Typical procedure

A 50 mL round - bottomed flsak was equipped with magnetic stirrer and charged with a solution of benzyl alcohol (1.0 mL, 0.01 mol) in CH_2Cl_2 (25mL). Complex (1) (13.0 g , 0.02 mol) was added in several portions within 15 min with vigorous stirring. The mixture was refluxed with stirring for 2h. The progress of the reaction was monitored by TLC(Aluminium oxide F254 - type E and

CCl_4/Et_2O in 3:1 as eluent). The mixture was diluted with CH_2Cl_2 (25mL) and filtered. The filtered solid was washed with CH_2Cl_2(2×25 mL) and the resulting filtrate was evaporated by a rotatory evaporator. The left liquid product was purified by column chromatography on silica gel(Type 60, Merck) using benzene/ethyl acetate (90/10) as eluent. Evaporation of the solvent afforded benzaldehyde. Yield (78%), IR(neat): ν =1694 cm^{-1}(C=O).

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