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COMPARISON OF FLUORO AND CHLOROCHROMATES (VI) AS ORGANIC OXIDANTS - A THERMOCHEMICAL APPROACH

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SUMMARY

The standard enthalpies of formation of pyridinium and potassium fluoro- and chloro- chromates (VI) have been determined from their heats of alkaline hydrolysis. The unexpected ability of pyridinium fluorochromate to oxidise organic substances almost as well as the chlorochromate is rationalized in terms of the close enthalpy values for the oxidising couples CrO_3F^-/F^- and CrO_3Cl^-/Cl^-. The oxidising ability of fluoroselenates relative to the Group VI analogues, the fluorochromates, is also assessed.

INTRODUCTION

Recently the existence of an isoelectronic series of reagents E_3AX_2 has been indicated, where E is a bonding or non-bonding electron pair, A a main-group V-VIII element and X a halogen [1,2]. These reagents are based on a trigonal bipyramidal geometry and their halogenating ability for a given X varies periodically with the central atom A. A corresponding tetrahedral series of oxidants, the tetra oxo- anions or neutral oxides, with the central atoms in Groups VI - VIII, have been used extensively in organic chemistry without explicit recognition of a similar periodicity in reactivity i.e. oxidising power moderating as a group is descended, or a period traversed from right to left. Of especial interest are the halo-substituted tetrahedral species because, in such series, one can investigate the variation in reactivity with change of the peripheral rather than the central atom. Also one can compare corresponding reagent pairs in A and B sub-groups. In particular the monofluoro and chloro-chromates (VI) have been popularized recently as mild but effective oxidants for converting primary or secondary alcohols to carbonyl compounds, and even of polycyclic arenes to quinones

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in high yields [3,4,5] it seems that the pyridinium fluoro and chlorochromates are very comparable in reactivity judging from the reaction conditions quoted. Reaction times, oxidant to substrate ratios, work-up and yields are similar. This seems surprising in view of the higher stability and stronger bonding in the fluoro-chromate anion. However, if corresponding reactions of fluoro and chloro-chromates are thermodynamically controlled and possess the same stoichiometry, then the reactivity should be related to thermochemical couples [1,2] rather than the energies of the reagent molecules alone. This hypothesis is tested with data obtained from heats of alkaline hydrolysis of fluoro and chloro-chromates.

EXPERIMENTAL

Reagents

Pyridinium and potassium fluoro and chlorochromates were prepared by published methods [3,5,6] and all salts were well dried in vacuo. A mid-fraction of pyridine, freshly distilled from potassium hydroxide, was used. Undistilled pyridine gave unstable salts presumably from internal oxidation of impurities.

Calorimetry

A 2.20M KOH solution served as the calorimetric medium. 50-100mgr. samples were inserted into 90ml of this medium using polythene syringes (1ml) with the Luer tip removed and stoppered with polythene bungs. A radio-active source was placed in the balance case to prevent any charging of the plastic syringes leading to weighing errors. Auxiliary heats of solution of K_2CrO_4, KCl, KF and pyridine were measured in the appropriate hydrolysates.

The isoperibol calorimeter was of the standard Dewar type but the measuring circuitry was of improved design. Briefly the Wheatstone bridge was replaced by a pseudo-bridge using a good quality operational amplifier across the ratio-arms and with the thermistor in the feed-back to the inverting terminal [7]. This arrangement gives a linear output with change in thermistor resistance unlike the Wheatstone bridge. The calibration heater timing was controlled by an I.C. timer (ZN 1034) accurate to 0.01%. The out of balance bridge voltage was transmitted from a digital voltmeter (Thurlby 1905a) to a computer for on-line processing of data.

Calibration of the calorimeter using the heat of solution of potassium chloride gave a value of -17.62 ± 0.05 kJ mol^{-1} in comparison with the accepted value of -17.59 kJ mol^{-1}.

The measured heats are summarized in the tables.

TABLE 1

Heats of reaction of chloro- and fluoro-chromates (VI) in 2.2M KOH

Salt	$-\Delta H$/kJ mol^{-1}
*$pyH^+CrO_3Cl^-$	126.5, 127.1, 126.6, 125.4 mean 126.4
$pyH^+CrO_3F^-$	128.7, 128.7, 129.9, 131.4, 128.5, 129.6, 128.5 mean 129.3
$KCrO_3Cl$	96.2, 98.4, 96.4, 95.7 mean 96.7
$KCrO_3F$	84.5, 87.0, 85.7, 86.4 mean 85.9

*py = pyridine

TABLE 2

Heats of solution of product molecules in hydrolysed salts.

Solute	in solutions of $PyH^+CrO_3Cl^-$	$KCrO_3F$	$KCrO_3Cl$
py	6.2 ± 0.2	n.p.	n.p.
KCl	-15.9 ± 0.1	n.p.	-15.9 ± 0.2
K_2CrO_4	-	-12.9 ± 0.3	-14.7 ± 0.1
KF	n.p.	19.3 ± 0.1	n.p.

n.p. not a hydrolysis product.

RESULTS AND DISCUSSION

Using the heats of hydrolysis (Table 1) and the auxiliary heats (Table 2) together with the following enthalpies ΔH_f° in kJ mol^{-1}
KOH (27.45 H_2O) -480.9; py (1) 101.2; H_2O -285.8; KF(c) -569.7
KCl(c) -436.5 and K_2CrO_4(c) -1404.4 [8,9,10] in the reaction equations

$$PyH^+CrO_3X^-(c) + 3KOH\ (aq) = K_2CrO_4(soln) + KX\ (soln) + py\ (soln) + 2H_2O$$

$$KCrO_3X(c) + 2\ KOH\ (aq) = K_2CrO_4(soln) + KX\ (soln) + H_2O$$

one obtains

$$\left.\begin{array}{lll} \Delta H_f^\circ & pyH^+CrO_3Cl^- & -975\ kJ\ mol^{-1} \\ " & pyH^+CrO_3F^- & -1144\ " \end{array}\right\}\ 169$$

$$\left.\begin{array}{lll} " & KCrO_3Cl & -1233\ " \\ " & KCrO_3F & -1390\ " \end{array}\right\}\ 157$$

As expected the fluoro-chromates are more stable than the corresponding chloro-chromates by about 160 kJ mol^{-1} The NBS 500 value quoted for $\Delta H_f^\circ KCrO_3Cl(c)$ of -1027 kJ mol^{-1} [8] is obviously incorrect since this value is only marginally more negative than the sum of the component KCl (c) and CrO_3(c) enthalpy values of -1016kJ mol^{-1} and this is hardly compatible with the stability of Peligot's salt.

The exact mechanism of halochromate oxidations has still to be elucidated, but the stoichiometry for a typical organic oxidation, that of octanol to octanal with $pyH^+CrO_3Cl^-$, has been established. It was found that the reaction could be completed at a 1/1 ratio of $pyH^+CrO_3Cl^-$/octanol rather than at the 1.25-1.50 ratios usually suggested [11]. This implies a 2e oxidation and subsequent reduction of Cr(VI) to Cr(IV) although the exact nature of this black residue was not examined. The product from $pyH^+CrO_3F^-$ oxidations appears similar and hence the overall reactions can be formulated as $pyH^+CrO_3X^- + RCH_2OH \rightarrow pyH^+X^- + CrO_2 + RCHO + H_2O$. Omitting the constant terms when X changes between F and Cl one can compare oxidative ability using the enthalpy couples

$\Delta H_f^\circ\ (pyH^+F^- - pyH^+CrO_3F^-)$ and
$\Delta H_f^\circ\ (pyH^+Cl^- - pyH^+CrO_3Cl^-)$

or because we do not have values for the pyridinium halides we can make a valid comparison using the enthalpies of the potassium salts. The fluoride couple obtained 820kJ mol^{-1} [-570 - (-1390)] is then only slightly less favourable than the chloride couple 796kJ mol^{-1} [-437-(-1233)] and hence provides a rationale for the unexpectedly small difference in reactivity.

A similar matching of chlorinating couples when covalent F replaces H has been encountered previously [2]. Again the difference is taken between two fluorine compounds rather than considering the fluorinated reagent alone.

$\Delta H^\circ_f(pFC_6H_4I$	-	$pFC_6H_4ICl_2)$		Δ
-81.7		-173.0	=	91.3
$\Delta H^\circ_f(C_6H_5I$	-	$C_6H_5ICl_2)$	=	92.8
114.5		21.7		

Fluoroselenates are the corresponding non-metallic analogues of fluorochromates in Group VI and using the above approach it should be possible to predict the oxidising ability of the former by comparing the relative values of the couples.

$SeO_3F^- \rightarrow SeO_2 + F^-$

and

$CrO_3F^- \rightarrow CrO_2 + F^-$

Again the absence of enthalpy values for fluoroselenates can be bypassed by using the athermal nature of F replacement by OH [12]. Enthalpies of H_2SeO_4, $HSeO_3F$ and SeO_2F_2 should be approximately the same For the chromium compounds this appears to hold. ΔH°_f CrO_2F_2 (c) -879, ΔH°_f $CrO_3(c) + H_2O(c)$ - 876 and ΔH°_f H_2CrO_4 $(1H_2O)$ -882.1 with a minimal heat of dilution ΔH°_f $H_2CrO_4 \infty H_2O$ -882.5.

Since the F^- is common to both couples it cancels in a difference, and the comparison is between ΔH°_f [H_2CrO_4 (c) or CrO_2F_2(c) - CrO_2 (c)] and ΔH°_f (H_2SeO_4(o) - SeO_2(c)). The former is 295kJ mol^{-1} the later 305kJ mol^{-1} indicating the similarity in oxidising ability of fluorochromates and selenates.

In practice there is no guarantee that oxidation reactions involving fluoroselenates would follow the same route as those using fluorochromates. These would be more difficult to handle because of their more rapid hydrolysis.

REFERENCES

1 M. Cartwright and A.A. Woolf, J.Fluorine Chem., 19 (1981) 101.

2 M. Cartwright and A.A. Woolf, Polyhedran 2 (1983) 811.

3 E.J. Corey and J.W. Suggs, Tetrahedron Lett., (1975), 2647.

4 G. Piancatelli, A. Scettri and M. D'Auria, Synthesis (1982) 245.

5 M.N. Bhattacharjee, M.K. Chaudhuri and H.S. Dasgupta, Synthesis, (1982) 588.

6 G. Brauer, 'Handbook of Preparative Inorganic Chemistry' 2nd edn, Vol. II p 1390, Academic Press, New York (1965).

7 B.H. Vassos and G. W. Ewing 'Analog and Digital Electronics for Scientists' 2nd edn., p 237, J. Wiley and Sons, New York (1980).

8 Selected Values of Chemical Thermodynamic Properties, National Bureau Standards Circular 500 (1950) and Tech. Notes 270-3, 270-4 (1969).

9 D.S. Barnes, CATCH Tables (Cr,Mo,W) Univ. of Sussex (1974).

10 CODATA Bulletin Key Values 28, (1978).

11 H.C. Brown, C.G. Rao and S.U. Kulkarni, J.Org.Chem., 44, (1979) 2809.

12 A.A. Woolf, J.Fluorine Chem., 11 (1977) 307.