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MICRO-REVIEW

Fluoroxysulphate: A Powerful New Oxidant, Kinetic Aspects

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In this review we highlight the recent work on the reaction chemistry of aqueous fluoroxysulphate.

Oxidations are of immense interest to a wide range of synthetic organic chemists. They play a vital role in the various oxidative transformations to specific transformation of different organic substrates and mechanistic studies are clearly a means of developing better synthetic methods. It is only in recent times that sufficient attention is being paid to the mechanistic aspects of oxidation in organic chemistry. Stoichiometric oxidations with metal oxidants such as permanganate[1] and chromic acid have been widely explored. Many liquid phase oxidants have been studied extensively employing relatively inexpensive sodium hypochlorite[2] and potassium peroxydisulphate oxidants in aqueous media[3]. The synthesis of the fluoroxysulphate ion, SO_4F^-, adds to a rather select list of aqueous oxidants. This review highlights the recent work on the reaction chemistry of aqueous fluoroxysulphate.

Stablity of Fluoroxysulphate Ion, SO_4F^-

The fluoroxysulphate is usually prepared in the form of its cesium salt, $CsSO_4F$, which is soluble in water to the extent of about 0.5 M at room temperature[4]. The half time for oxidation of water by the fluoroxysulphate ion increases from about 15 min at room temperature to about 3.6 h at the ice point[5]. The half reaction

$$SO_4F^- + 2H^+ + 2e^- \rightleftharpoons HSO_4^- + HF$$

has a standard electrode potential of 2.47 V,[6] making fluoroxysulphate thermodynamically a somewhat less potent oxidant.

Aqueous solutions of fluoroxysulphate are unstable. They decompose gradually with the evolution of varying amounts of O_2. The acidity of the final solution is considerably lower than would result from the reaction

$$SO_2F^- + H_2O \rightarrow HSO_4^- + HF + \frac{1}{2}O_2$$

and it is likely that substantial quantities of SO_4F^- are formed.

In alkaline solution, the decomposition of fluoroxysulphate is essentially

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instantaneous. A transient yellow colour is frequently observed, and a pungent odour is detected.

Standardisation of SO_4F^-

Fluoroxysulphate ion can be analysed iodometrically. The oxidising titres of the salt can be determined by dissolving weighed amounts in a potassium iodide solution, acidifying and titrating the liberated I_3^- immediately with standard thiosulphate solution to a stach end point[7]. This method is only entirely accurate for freshly prepared solutions, since the reaction of fluoroxysulphate with water produces some peroxymonosulphate SO_4OH^- and lesser amounts of hydrogen peroxide, both of which oxidise iodide[5].

Method of preparation

The fluoroxysulphate ion is usually prepared in the form of its cesium salt, $CeSO_4F$, by fluorination of aqueous cesium sulphate.[8] A 20% mixture of fluorine in nitrogen was passed through 2 M solution of Ce_2SO_4 in Tefzel tube over the course of 1 h at temperature between 0 and –5°C.[7] The yellowish-white solid precipitates out. It is centrifuged, washed with a little water, and dried *in vacuo* without heating.

Aqueous decomposition of fluoroxysulphate

The hydrolysis of the fluoroxysulphate is a complex process producing peroxymonosulphate, hydrogen peroxide and oxygen. The overall stoichiometry in acid solution may be represented by the equations:

$$SO_4F^- + H_2O \rightarrow HSO_5^- + HF$$

$$SO_4F^- + H_2O \rightarrow SO_3F^- + H_2O_2$$

$$2SO_4F^- + H_2O \rightarrow HSO_4^- + SO_3F^- + HF + O_2$$

The formation of HSO_5^- may be rationalised in terms of nucleophilic substitution of OH^- for F^-:

$$SO_4F^- + H_2O^* \rightarrow SO_4O^*H + HF$$

The O^{18} experiment shows that the HSO_5^- produced contains a solvent oxygen atom as the terminal atom in the peroxy moiety. This experiment further indicates that both H_2O_2 and O_2 produced contain one oxygen atom from the solvent and one from the fluoroxysulphate. This, in conjnuction with the measurement of H^+ evolution, would imply that the H_2O_2 is formed by transfer of oxygen from SO_4F^- to H_2O:

$$SO_4F^- + H_2O^* \rightarrow HOO^*H + SO_3F^-$$

and that the O_2 results from subsequent oxidation of the H_2O_2.

$$SO_4F^- + H_2O_2 \rightarrow HSO_4^- + HF + O_2$$

A mechnism is proposed in which the rate determining steps are the interaction of SO_4F^- with water to form HSO_5^- and $H_2O_2^5$:

$$SO_4F^- + H_2O_2 \rightarrow SO_4^- + HO_2 + HF$$

$$SO_4^- + H_2O \rightarrow HSO_4^- + OH$$

$$OH + H_2O_2 \rightarrow HO_2 + H_2O$$

$$HO_2 + SO_4F^- \rightarrow SO_4^- + HF + O_2$$

$$SO_4^- + HO_2 \rightarrow HSO_4^- + O_2$$

This is similar to the mechanism proposed to explain the reaction between $S_2O_8^{2-}$ and H_2O_2.[9]

Fluoroxysulphate Ion, SO_4F^-: A one or two electron oxidant

Of particular interest concerning the reaction of this powerful oxidising agent is the question of whether they act as one or two-electron oxidant.

Aqueous fluoroxysulphate appears to react primarily as one-electron oxidant. Thompson and Appleman[5] have suggested an F atom transfer mechanism with a number of aqueus reductants:

$$SO_4F^- + R \rightarrow SO_4^- + RF$$

$$SO_4^- + R \rightarrow SO_4^{2-} + R^+$$

They obtained positive evidence for one-electron oxidation path from the observation that the reaction of fluoroxysulphate with Cr(II) produce an approximately equimolar mixture of hexaquochromium(III) and fluorochromium(III).

$$SO_4F^- + Cr^{2+} \rightarrow SO_4^{4-} + CrF^{2+}$$

$$SO_4^{4-} + Cr^{2+} \rightarrow SO_4^{2-} + Cr(III)$$

This scheme is analogous to that proposed for the oxidation of Cr^{2+} by $S_2O_8^{2-}$, the difference being that transfer of F atom from SO_4F^- takes the place of transfer of SO_4^- from $S_2O_8^{2-}$.[10]

The oxidation of Pu(III) by fluoroxysulphate also probably proceeds with one electron path.

Although fluoroxysulphate appears formally to be two electron oxidant, many of its reactions follow the one-electron mechanism.

Kinetic Aspects of Oxidation by Fluoroxysulphate

Aqueous solutions of fluoroxysulphate are very powerfully oxidising. Chloride, bromide and iodide are oxidised first to the free halogens and then to higher states. Vanadium (IV) is oxidised to vanadium (V), Ce(III) to Ce(IV) and Co(II) to Co(III). Manganous ion is oxidised first to Mn(III) and then to permangante. Pb^{2+}, Tl^+ and Ag^+ are all oxidised. However, Cr(III) is not oxidised in acidic solution. In alkaline media, chromate is formed. It reacts vigorously with aqueous hydrazoic acid to produce a mixture of N_2, N_2O and N_3F. Fluoroxysulphate, in general, is a more rapid oxidant than peroxymonosulphate.

Fluoroxysulphate readily transfers oxygen to water. It reacts rapidly with free and coordinated ClO_2^-, with Cr_2^+ and with I^-. Oxygen transfer to ClO_2^- yields chlorate as a stable product. The reaction of $Co(NH_3)_5ClO_2^{2+}$ with SO_4F^- is complex and would probably give $Co(NH_3)_5ClO_3^{2+}$ as a result of oxygen transfer to $Co(NH_3)_5ClO_2^{2+}$. Oxygen transfer to Cr^{2+} forms Cr(IV) and ultimately leads to the production of polynuclear Cr(III) species.

The reaction of $Co(NH_3)_5ClO_2^{2+}$ with SO_4F^- may proceed either by 1-equivalent or 2-equivalent oxidation of the ClO_2^- as given below in mechanism I and mechanism II:

Mechanism I

$$SO_4F^- + Co(NH_3)_5ClO_2^{2+} \rightarrow SO_4^- + Co(NH_3)_5ClOF^{2+}$$

$$Co(NH_3)_5ClO_2F^{2+} \rightarrow Co(NH_3)_5F^{2+} + ClO_2$$

$$SO_4^- + Co(NH_3)_5ClO_2^{2+} \rightarrow SO_4^{2-} + Co(NH_3)_5ClO_2^{3+}$$

$$Co(NH_3)_5ClO_2^{3+} + H_2O \rightarrow Co(NH_3)_5H_2O^{3+} + ClO_2$$

$$SO_4^- + ClO_2 \rightarrow SO_4^{2-} + ClO_2^+$$

$$ClO_2^+ + H_2O \rightarrow ClO_3^- + 2H^+$$

Mechanism II

$$SO_4F^- + Co(NH_3)_5ClO_2^{2+} \rightarrow SO_4^{2-} + Co(NH_3)_5ClO_2F^{3+}$$

$$Co(NH_3)_5ClO_2F^{3+} + H_2O \rightarrow Co(NH_3)_5H_2O_3^+ + ClO_2F$$

$$\rightarrow Co(NH_3)_5F^{2+} + ClO_3^- + 2H^+$$

$$ClO_2F + Co(NH_3)_5ClO_2^{2+} + H_2O \rightarrow Co(NH_3)_5H_2O^{3+} + 2ClO_2 + F^-$$

$$ClO_2F + H_2O \rightarrow ClO_3^- + HF + H^+$$

A similar choice of mechanism exists for the oxidation of free chlorite by fluoroxysulphate. Mechanisms III and IV are possible.

Mechanism III

$$SO_4F^- + ClO_2^- \rightarrow SO_4^- + ClO_2 + F^-$$

$$SO_4^- + ClO_2^- \rightarrow SO_4^{2-} + ClO_2$$

$$SO_4^- + ClO_2 \rightarrow SO_4^{2-} + ClO_2^+$$

Mechanism IV

$$SO_4F^- + ClO_2^- \rightarrow SO_4^- + ClO_2F$$

$$ClO_2F + ClO_2^- \rightarrow 2ClO_2 + F^-$$

$$ClO_2F + H_2O \rightarrow ClO_3^- + HF + H^+$$

It is interesting to note that species that is reactive towards fluoroxysulphate is ClO_2^- rather than $HClO_2$. Apparently the increased electron density on the chlorite anion outweighs the electrostatic repulsion between it and SO_4F^-

A similar mechanism operates for the oxidation of I^- which is given in mechanisms V and VI

Mechanism V

$$SO_4F^- + I^- \rightarrow SO_4^- + IF^-$$

$$SO_4^- + I^- \rightarrow SO_4^{2-} + I$$

$$IF^- + I^- \rightarrow I_2^- + F^-$$

$$I + I^- \rightarrow I_2^-$$

$$2I_2^- \rightarrow I_3^- + I^-$$

Mechanism VI

$$SO_4F^- + I^- \rightarrow SO_4I^- + F^-$$

$$SO_4I^- + H_2O \rightarrow SO_4^{2-} + HOI + H^+$$

$$H^+ + HOI + I^- \rightarrow I^2 + H_2O$$

It would be interesting to study the reaction of SO_4F^- with 2-equivalent reductants such as sulphite and bromate to determine if the reactions involve transfer of fluoroxysulphate oxygen.

Ag(I) Catalysed Oxidation by Aqueous Fluoroxysulphate

The oxidation of Co^{2+} and VO^{2+} by aqueous fluoroxysulphate in the absence of silver(I) is very slow. Some reducing agents as Cr^{3+} are not oxidised at all. However, the oxidation reactions are accelerated in the presence of Ag(I). The kinetic and stoichiometric results of studies of the Ag(I) catalysed oxidation of Cr^{3+} show the following stoichiometries:

$$2Cr^{3+} + 3SO_4F^- + 8H_2O \rightarrow 2HCrO_4^- + 3HSO_4^-$$

$$2VO^{2+} + SO_4F^- + 2H_2O \rightarrow 2VO_2^+ + HSO_4^- + HF + 2H^+$$

$$2Co^{2+} + SO_4F^- + 2H^+ \rightarrow 2Co^{3+} + HSO_4^- + HF$$

The pseudo first order rate constants in all the three systems appear to be directly dependent on the Ag(I) concentration and nearly independent of the concentration of reductant, in accordance with the rate law

$$-d[SO_4F^-]/dt = k[Ag^+][SO_4F^-]$$

The values of k and the corresponding activation are the same for all three systems, the rate determining step for all three catalysed reactions is the biomolecular oxidation of Ag^+ by SO_4F^-.

$$SO_4F^- + Ag^+ \rightarrow SO_4^- + Ag^{2+} + HF$$

Both SO_4^- and Ag^{2+} may be effective in oxidising the reducing substrate, and the SO_4^- may also produce more Ag^{2+} from Ag^+.[11]

The reaction schemes proposed in the case of Ag(I) catalysed fluoroxysulphate oxidation are very much similar to those proposed for the corresponding Ag^+ catalysed oxidations by peroxydisulphate.[12]

Conclusion

The most surprising feature of the aqueous chemistry of fluoroxysulphate is the enormous selectivity displayed by this oxidant in the reaction with reducing substrates. The fluoroxysulphate ion shows this selectivitiy despite its formidable thermodynamic oxidising pair.[7]

The relative reactivities toward SO_4F^- of the reductants that have been studied to date stand in the order $Ag^+ \gg Co^{2+} > VO^{2+} > H_2O > Cr^{3+}$. These studies indicate that the thermodynamic driving force is not a major factor in determining these reactivities.

Fluoroxysulphate is the first known example of an ionic hypofluorite. Its ionic character is of special significance in that it permits the formation and isolation of relatively stable salts. The stability of these salt, along with their ease of preparation and unusual reactivity, may well make the fluoroxysulphates uniquely useful synthetic and analytical reagents for both inorganic and organic chemistry.

REFERENCES

1. K.B. Wiberg, Oxidation in Organic Chemistry, Academic Press, New York, p. 247 (1965).
2. R.A. Sheldon and J.K. Kochi, Metal Catalysed Oxidation of Organic Compounds, Academic Press, New York (1983).
3. D.A. House, *Chem. Revs.*, **62**, 185 (1962).
4. W.V. Steel, P.A.G. O'Harc and E.H. Appleman, *Inorg. Chem.*, **20**, 1022 (1981).
5. R.C. Thompson and E.H. Appleman, *Inorg. Chem.*, **19**, 3248 (1980).
6. P.A.G. O'Harc, H.E. Flotov and E.H. Appleman, *J. Chem. Thermody.*, **14**, 1191 (1982).
7. E.H. Appleman, L.J. Basile and R.C. Thompson, *J. Am. Chem. Soc.*, **101**, 3384 (1979).
8. E.H. Appleman, *Inorg. Synth.*, **24**, **22** (1986).
9. M.S. Tsao and W.K. Wilmarth, *Discuss. Faraday Soc.*, **29**, 137 (1960).
10. E.E. Pannington and A. Haim, *J. Am. Chem. Soc.*, **90**, 3700 (1968).
11. C. Walling and D.M. Camaioni, *J. Org. Chem.*, **43**, 3266 (1978)
12. W.K. Wilmarth and A. Haim, in: J.O. Edwards (Ed.), Peroxide Reaction Mechanism, Interscience, New York, p.194 (1962).

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