than 4 favour polymeric species except when a large orthosubstituent is present. However, high values of the moments observed in some of the complexes are likely to be associated with steric hindrance.

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REFERENCES

- 1. J. Lewis and R. C. Thompson, Nature 200, 468 (1963).
- 2. J. Lewis, Y. C. Lin, L. K. Royston and R. C. Thompson, J. Chem. Soc. 6464 (1965)
- 3. J. Lewis, F. E. Mabbs, L. K. Royston and W. R. Smail, J. Chem. Soc. 291 (1969).
- 4. C. S. Fountain and W. E. Hatfield, Inorg. Chem. 4, 1368 (1965).
- 5. S. Yamada, H. Nishikawa and S. Miki, Bull. Chem. Soc. Japan 37, 576 (1964).
- 6. R. A. Zelonka and M. C. Baird, Inorg. Chem. 11, 134 (1972).
- 7. G. Kortum, W. Vogel and K. Andrussow, Dissociation Con-

*Author to whom correspondence should be addressed.

J. inorg. nucl. Chem. Vol. 43, pp. 1947-1948, 1981 Printed in Great Britain.

- 8. J. M. Wilson, N. E. Gore, J. E. Sawbridge and F. Cardenas-Cruz, J. Chem. Soc. B, 852 (1967).
- 9. A. I. Vogel, A Textbook of Practical Organic Chemistry, 3rd Edn, pp. 163-179. Longmans, London (1961).
- 10. G. Schwarzenbach, Helv. Chim. Acta 29, 1338 (1946).
- 11. K. S. Patel and P. O. Ikekwere, J. Inorg. Nucl. Chem. 41, 51 (1981).
- 12. P. O. Ikekwere and K. S. Patel J. Inorg. Nucl. Chem. (in press).
- 13. M. Kato, H. B. Jonassen and J. C. Fanning, Chem. Rev. 64, 99 (1964).
- 14. E. A. Boudreaux, Inorg. Chem. 3, 506 (1964).
- 15. E. Spinner, J. Chem. Soc. (B), 874 (1967).
- 16. J. H. S. Green, Spectrochim. Acta 33A, 575 (1977).
- 17. J. R. Wasson, Chin-I Shyr and C. Trapp, Inorg. Chem. 7, 469 (1968).
- 18. J. Catterick and P. Thornton, Adv. Inorg. Chem. Radiochem. 20, 291 (1977).
- 19. G. A. Popovich, A. V. Ablov, Yu. V. Yablokov and G. Kiosse, Russ. J. Inorg. Chem. 16, 316 (1971).
- 20. Yu. V. Yablokov and A. V. Ablov, Dokl. Akad. Nauk. SSSR, 144, 173 (1962).
- 21. H. M. Swartz, J. R. Bolton and D. C. Borg (Eds), Biological Applications of Electron Spin Resonance, pp. 50. Wiley, New York (1972).
- 22. G. A. Popovich and K. M. Mirel, Russ. J. Inorg. Chem. 17, 978 (1972).

ibria in such solutions, the calculated concentrations are ap-

RESULTS AND DISCUSSION

reaction. Similar results are found in the absence of sulfate. The

second order rate decreases with increasing acidity and this may

be ascribed to the decrease in sulfate concentration due to the

The energy of activation of 21.5 kcal/mol in the presence of

The Tl(III) oxidation of Fe(II) in presence of sulfate is first order in each reactant and the product iron(III) retards the

TI(III) oxidation of Fe(II) in presence of sulfate

(Received 24 July 1980; received for publication 14 November 1980)

proximate.

sulfate-bisulfate equilibrium.

The Tl(III) oxidation of Fe(II) has been studied[1,2] but its catalysis by sulfate noted early[1] has not received any detailed attention. In view of the distinctive effects of anions such as chloride[3] and the sulfate catalysis of other Tl(III) oxidations[4], the reaction is of interest.

EXPERIMENTAL

TI(III) perchlorate, obtained as previously[1], was standardised with EDTA[5] and Fe(II) with dichromate[6]. In the kinetic runs, at ionic strength 4 and acidity 0.5 M, these were maintained constant with sodium perchlorate and perchloric acid. For most runs 2[TI(III)] = [Fe(II)] = 0.005 M, except when the reaction order was being examined. Save when its effect was under observation, the (lithium) sulfate concentration was constant at 0.4 M. The reaction was followed by back titration of excess standard cerium(IV), added at different intervals to aliquots of the reaction solution, with standard Fe(II). Rates, which were reproducible within 4 percent, were measured at 0°C and for obtaining activation parameters at three more temperatures. The dielectric constant of the reaction medium was varied by having different proportions by volume of dioxane. In these experiments the ionic strength was constant at 1.735. The actual sulfate concentrations in solution were calculated from the added sulfate and the sulfate-bisulfate equilibrium constant of 0.12[7]. The $TISO_4^+$ and $TI(SO_4)_2^-$ in solution were calculated from the dissolved Tl(III), added sulfate and the respective equilibrium constants [7]. The remaining Tl(III) was taken as Tl^{3+} for use in Fig. 1. The fractions α_0 , α_1 and α_2 plotted against log [SO₄²⁻] in Fig. 1 represent the fractions of the Tl(III) present as Tl³⁺, $TISO_4^+$ and $TI(SO_4)_2^-$ respectively. In view of the multiple equil-





0.4 M sulfate is not much different to the case where no sulfate is present, but the entropy of activation of + 12 e.u. is very much different from the value, -7 e.u., in the absence of sulfate. Although it is not possible to interpret satisfactorily this large difference in entropy change especially in view of the high ionic strength used, it may nevertheless indicate changes in the reactants and activated complex in the presence of sulfate. Furthermore, as the dielectric constant of the medium decreases from 3.76×10^{-2} to 17.3×10^{-2} I mol⁻¹ s⁻¹ ($\mu = 1.735$, H⁺ = 0.5 M, [SO₄²⁻] = 0.4 M and 2[T1³⁺] = [Fe²⁺] = 0.005 M), a result normally expected for a reaction between oppositely charged ions[8]. In contrast, when no sulfate was present, no appreciable change in rate occurred even in 30% dioxane in water (v/v).

The influence of sulfate at an ionic strength of 4 and acidity of 0.5 M is shown in Fig. 1. The log k_2 vs log $[SO_4^{2-}]$ graph shows a steep increase of rate in the sulfate concentration range of 0.02–0.2 M, reaching a maximum thereafter. The maximum at high sulfate suggests that sulfate does more than simply take part in the formation of the activated complex. The experimental results become clear if it is assumed that the species responsible for the acceleration is the sulfate complex of Tl(III), Tl(SO_4)_2^-, which forms with facility in aqueous media as evidenced by the high stability constant[7]. Complexes such as TlSO_4^+, TlOH²⁺ appear to be less important. When the fractions of Tl³⁺, TlSO_4^+ and Tl(SO_4)_2^- of total Tl(III), α_0 , α_1 and α_2 respectively, are plotted against log $[SO_4^{2-}]$ as in Fig. 1, it is seen that the fraction of Tl(SO_4)_2^- attains a maximum which corresponds to the maximum of Tle k_2 vs log $[SO_4^{2-}]$ curve. It may therefore be inferred that the main oxidant in presence of appreciable sulfate

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concentrations is $Tl(SO_4)_2^-$ and the mechanism may be written as

Such a mechanism is compatible with the rate increase in the presence of sulfate being almost entirely due to the entropy factor, the activation energy not changing much. Sulfate catalysis in other Tl(III) oxidations may also be due to the oxidant being $Tl(SO_4)_2^{-1}$.

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REFERENCES

- 1. C. E. Johnson, Jr., J. Am. Chem. Soc. 74, 959 (1952).
- 2. K. G. Ashurst and W. C. E. Higginson, J. Chem. Soc. 3044 (1953).
- 3. F. R. Duke and B. Bornong, J. Phys. Chem. 60, 1015 (1956).
- C. H. Brubaker and J. P. Mickel, J. Inorg. Nucl. Chem. 4, 55 (1957); A. C. Harkness and J. Halpern, J. Am. Chem. Soc. 81, 3526 (1959).
- 5. R. Pribil, V. Vesely and K. Kratochvil, Talanta 8, 52 (1961).
- 6. Vogel's Textbook of Quantitative Inorganic Analysis (4th Edn), p. 360. ELBS-Longman (1978).
- F. Ya. Kul'ba, Yu. B. Yakovlev and V. E. Mironov, *Zh. Neorg. Khim.* 10, 2044 (1965).
- 8. A. A. Frost and R. G. Pearson, Kinetics and Mechanism, p. 142. Wiley, New Delhi (1970).

J. inorg. nucl. Chem. Vol. 43, pp. 1948-1949, 1981 Printed in Great Britain. 0022-1902/81/081948-02\$02.00/0 Pergamon Press Ltd.

A study of the precipitates formed by hydrolysis of Fe(III) nitrate solution containing Na⁺ and SO₄²⁻

(Received 6 June 1980; received for publication 5 November 1980)

We have been investigating the chemical nature of the hydrolysis products precipitated in 0.1 M solutions of various Fe(III) salts at pH 1.5 \sim 1.8 by Mössbauer spectrometry and X-ray diffractometry. It has been found that the products varied as the anion present in the solution varied. When an Fe(III) salt solution, containing Na⁺ and SO₄²⁻, was warmed at 353 K for 3 hr, NaFe₃(SO₄)₂(OH)₆ was precipitated [1].

If the solution temperature was raised to 363 K or to the boiling point, the proportion of α -FeOOH in the hydrolysis product increased. This was shown both by X-ray diffractometry and Mössbauer spectrometry. The chemical states and the formation process of the precipitates are discussed in this report.

EXPERIMENTAL

The hydrolysis of Fe(III) was carried out in the same way as described in the previous report[1]. The Fe(III) solutions were prepared by adding 1.42 g of Na_2SO_4 to 200 ml of a 0.1 M Fe(III) nitrate solution and warming to 353 K, 363 K or the b.p. for 3 hr to promote the hydrolysis. The precipitates formed were separated by the centrifugation (10,000 G) and dried at room temperature. Mössbauer spectra of the hydrolysis products were taken with a conventional constant-acceleration spectrometer at room temperature.

RESULTS AND DISCUSSION

The precipitates formed at 353 K, 363 K and the b.p. were identified as NaFe₃(SO₄)₂(OH)₆, a mixture of NaFe₃(SO₄)₂(OH)₆ and α -FeOOH and α -FeOOH, respectively, by their X-ray diffraction patterns. Crystallinity of the α -FeOOH was poor because the X-ray diffraction peaks were weak and broad compared with those of α -FeOOH produced in a conventional way such as α -FeOOH prepared by the transformation of Fe(III) hydroxide in an alkaline solution, or by the hydrolysis of Fe(III) nitrate solution at 353 K. Mössbauer spectra of the precipitates are shown in Fig. 1(a-c). The α -FeOOH was found superparamagnetic as was consistent with the X-ray diffraction results. The diameter of the superparamagnetic α -FeOOH particles was estimated as less than 500 A referring to the data presented by Shinjo[2].

The isomer shifts (δ) of the NaFe₃(SO₄)₂(OH)₆ and α -FeOOH are 0.356 ± 0.023 mms⁻¹ and 0.368 ± 0.023 mms⁻¹ with reference to an α -iron foil, respectively, showing that iron atoms are present in the trivalent state. The quadrupole splitting (Δ) of the NaFe₃(SO₄)₂(OH)₆ and α -FeOOH are 1.149 ± 0.023 mms⁻¹ and 0.528 ± 0.023 mms⁻¹, respectively. As the velocity range extended to ±2 mms⁻¹, these values are precise compared with those reported in the previous paper[3]. The Δ of α -FeOOH is com-