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The Significance of the Absence of Evidence of Chelation in the Functioning of Salicylate Ion as a Bridging Ligand for Electron Transfer between Ruthenium(III) and Titanium(III)
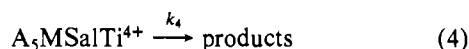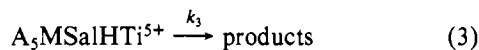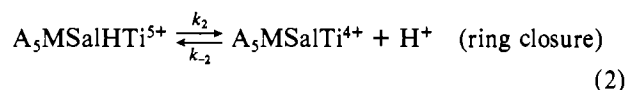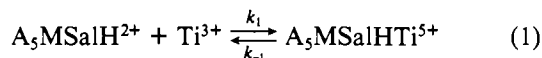
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Martin and Gould[1] have shown that the acid dependence of the rate of reaction between Ti(III) and several salicylato complexes of Co(III) indicates that chelation of Ti(III) to the bridging ligand occurs prior to electron transfer (ET). We now report data that demonstrate that a different mechanism operates in the reduction of a corresponding complex of ruthenium(III).

(Salicylato)pentaammineruthenium(III) perchlorate was prepared with use of the method of Stritar and Taube.[2] Anal. Calcd for $[Ru(NH_3)_5C_7H_6O_3]ClO_4$: Ru, 19.3, C, 16.1; N, 13.4; H, 3.8. Found: Ru, 19.1; C, 15.9; N, 13.6; H, 3.7.[3,4] The UV–visible spectrum showed peaks at 410 ($\epsilon = 245$ M^{-1} cm^{-1}) and 295 nm ($\epsilon = 6030$). The complex gave a formal redox potential of 55 mV vs. NHE (cyclical voltammetry at pH 1.5 in 1 M LiCl). Reduction[5] of the complex by Ti(III) gave a second-order rate constant of $(6.3 \pm 0.1) \times 10^2$ M^{-1} s^{-1} independent of [H+] over the range tested [H+] (0.4 – 0.12 M in 1 M LiCl at 25.0 °C). This acid-independent second-order rate constant is similar to the value determined[5] for $Ru(NH_3)_5OOCCH_3^{2+}$ (7.0×10^2 M^{-1} s^{-1}) and for[6] $Ru(NH_3)_5NCS^{2+}$ (8.1×10^2 M^{-1} s^{-1}).

The results can be discussed on the basis of the mechanism

$$A_5MSalH^{2+} + Ti^{3+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A_5MSalHTi^{5+} \qquad (1)$$

$$A_5MSalHTi^{5+} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} A_5MSalTi^{4+} + H^+ \quad \text{(ring closure)} \qquad (2)$$

$$A_5MSalHTi^{5+} \overset{k_3}{\longrightarrow} \text{products} \qquad (3)$$

$$A_5MSalTi^{4+} \overset{k_4}{\longrightarrow} \text{products} \qquad (4)$$

When M = Co the data indicate that one of the factors determining the rate is a competition between ET within a deprotonated and chelated intermediate (reaction 4) and proton-assisted decomposition of that intermediate (the reverse of reaction 2). no such complication occurs when M = Ru, indicating a fundamental change in mechanism.[6]

The measured reduction potential and data on related systems[8] leads to the estimate $k_{11} = 3 \times 10^4$ M^{-1} s^{-1} for the electron-exchange rate constant of the Ru(III)–Ru(II) couple of interest. Combining this estimate with the estimate of the Ti^{4+}/Ti^{3+} electron-exchange rate constant given by Brunschwig and Sutin[9] leads to a predicted outer-sphere redox rate constant of $k_{12} \approx 0.6$ M^{-1} s^{-1} for the present reaction. taking a value of 0.01 M^{-1} for the ion-pair (or encounter) complex

formation constant appropriate to that reaction yields a first-order rate constant of ~ 60 s^{-1} for outer-sphere Ru(III)–Ti(III) ET.

Diebler[10] has found that the rate constant for substitution of acetate onto (acetato)titanium(III) is $k_1 \approx 10^7$ M^{-1} s^{-1}. Using a value of 10^0 M^{-1} for the ion-pair formation constant for this process leads to a value of 10^7 s^{-1} for the first-order rate constant for water loss from Ti(III). The labilizing effect of a carboxyl group which is already coordinated to Ru(III) would be expected to be less than that of acetate ion.[11] This leads to the estimate of $k_2 \approx 10^5$ s^{-1}.

The lack of a [H+] dependence in the M = Ru case implies either $k_3 > k_2$ or $k_4 > k_{-2}[H^+]$. On the basis of equilibrium measurements on the Fe(III) complex,[12] it appears that $k_2 \approx k^{-2}[H^+]$, so that on either basis k_{ET} $(=k_3$ or $k_4) > 10^5$ s^{-1}. The divergence between $K > 10^5$ s^{-1} (inner-sphere ET) and $K \approx 60$ s^{-1} (outer-sphere ET) is consistent with greater cross–bridge electronic interaction in the inner-sphere case. The divergence between the results with M = Co and M = Ru is consistent with the expectation that cross-bridge electronic interaction through the π system of the carboxylate bridge is greater in the t_{2g}–t_{2g} case (Ru(III)–Ti(III)) than in the e_g–t_{2g} case (Co(III)–Ti(III)).

Registry No. $[Ru(NH_3)_5C_7H_6O_3]ClO_4$, 77744-87-7; Ti^{3+}, 22541-75-9.

(10) Diebler, H., private communication.
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Ammonolysis of Bis(trifluoromethyl)phosphine: A Source of New Chiral Phosphines

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A paper presented at a recent meeting[1] described some new products obtained by the reaction of $(CF_3)_2PH$ with trimethylamine: bis(phosphino)methanes, $R(CF_3)PP(CF_3)_2$ compounds (where R is CHF_2, CH_2F, or CH_3), and other phosphines derived from their P–P bond cleavage reactions. Of the whole list, the compounds most difficult to obtain in good yields and purity were $CHF_2(CF_3)PCl$ and $CH_2F(CF_3)PCl$; they were identified only by their NMR spectra and further chemistry. Thus it seemed useful to repeat the action of ammonia on $(CF_3)_2PH$, which had been reported to lead through CF_3PCF_2 to $CHF_2(CF_3)PNH_2$, convertible to $CHF_2(CF_3)PCl$ by action of HCl.[2] Table I presents the stoichiometry of three such experiments.

For experiment 1 the reactants, in a 40-mL stopcocked tube, were warmed from −130 to −110 °C during 60 min, then quickly to −70 °C, and to −50 °C in 5 min. The volatiles were

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(1) A. B. Burg, Abstracts of the 2nd Chemical Congress of the North American Continent, Division of Fluorine Chemistry, Paper No. 12, 1980.
(2) H. Goldwhite, R. N. Haszeldine, and D. G. Rowsell, *J. Chem. Soc. A*, 6878 (1965).