reacts with DTT to give a quantitative yield of TiO_2; the ligand is quantitatively isolated as toluene (u.v. spectrum, quantitative measurements).

The thermal effect of DTT oxidation was 514.56 ± 19.26 kJ mol^{-1}, as calorimetric method showed. Considering the thermal effect of titanium oxidation to TiO_2 to be 942.03 kJ/g. at., it is possible to estimate the metal-ring bond average energy, *viz*, 213.53 ± 9.63 kJ mol^{-1}.

The electronic absorption spectrum of the DTT hexane solution has two well pronounced bands. The u.v. high intensity band ($\lambda_{1max} = 362$ nm, $\varepsilon_{1max} = 2.9 \times 10^4 l \cdot mol^{-1} \cdot cm^{-1}$) may be assigned to charge transfer and a weak band in the visible region ($\lambda_{2max} = 508$ nm, $\varepsilon_{2max} = 3.5 \times 10^2 l \cdot mol^{-1} \cdot cm^{-1}$) to a d–d transition.

The i.r. spectrum of DTT is shown in Figure 2. The band assignments were based upon those for dibenzenetitanium(2).

An investigation showed DTT to be effective as an alkene and alkyne polymerization catalyst, like DBT(2). DTT does not react with pure ethylene. We observed formation of polyethylene using ethylene containing 10^{-3}% vol. of oxygen.

Reaction was carried out at 25 °C in a 200 cm^3 metal vessel using 50 cm^3 of a DTT solution ($c = 2.5 \times 10^{-3} mol \cdot l^{-1}$). The pressure of monomer was maintained at 10 atm and the solution was stirred.

The initial reaction rate was $5.2 \times 10^{-4} mol \cdot dm^{-3} \cdot s^{-1}$. The yield of polyethylene in two hours was 0.6 kg/g · Ti. The molecular weight of polymer formed was 1200000; the m.p. 143 °C.

DTT reacted with styrene to form polystyrene (polymer yield 400 g/g · Ti in two hours).

The polymerization of acetylene started immediately after introducing the monomer (p = 1 atm) and stopped spontaneously after *ca.* 3 min. A mixture of *cis-* and *trans-*isomers was formed. The maximum yield of polymer was 120 g/g · Ti.

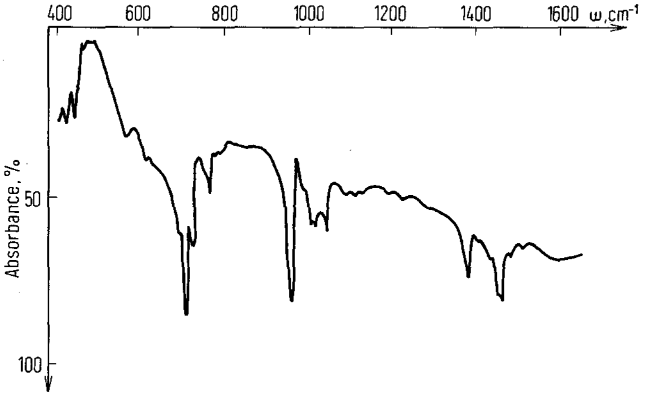

Figure 2. I.r. absorption spectrum of DTT. The sample was prepared by depositing DTT on a KBr monocrystal from toluene solution.

DTT polymerizes phenylacetylene (polymer yield 250 g/g · Ti in two hours); the reaction conditions are identical to those in(2).

The mechanism of these catalytic reactions is under study.

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Reaction of an Ethylenediaminetetraacetatoiron(III) Complex with Cyanide Ion

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The substitution of multidentate ligands complexed to metal ions by monodentate ligands has evoked the interest of many workers. The substitution of polyaminocarboxylates by cyanide ion in their complexes of nickel(II) has been studied extensively(1). The polyaminocarboxylate complexes of cobalt(II)(2, 3) and manganese(III)(4) have also received attention, however no investigation has so far been reported about the reaction of polyaminocarboxylate complexes of iron(III) with cyanide ion.

In this communication we report the kinetics and mechanism of reaction of cyanide ion with an ethylenediaminetetraacetato complex of iron(III), which is belived to be a seven coordinated species, having one water molecule in the solid state(5) and in neutral or acidic conditions, and which looses a proton in the presence of base to give FeY(OH) species (Y = EDTA). The reaction was studied spectrophotometrically at 395 nm [λ_{max} (product) *viz.*, the $Fe(CN)_5(OH)$ complex(6)] at pH = 10.5, temp. = 25 °C and $\mu = 0.25$ M ($NaClO_4$). Under pseudo first order conditions, using an excess of cyanide, the reaction was found to be first order with respect to metal complex and to exhibit an order with respect to

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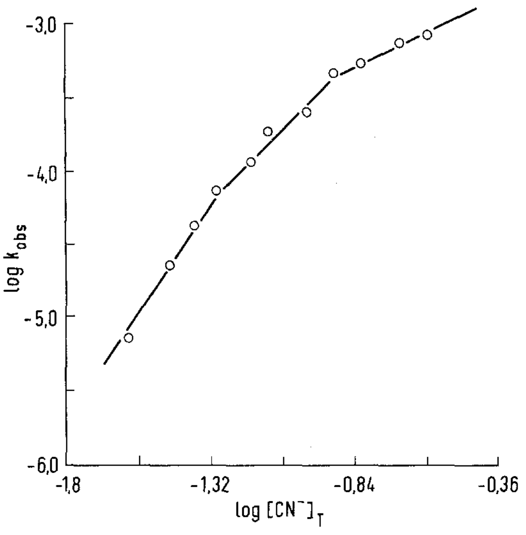

Figure 1. Cyanide dependence of the observed pseudo first order rate constants in the reaction of cyanide ion with Fe(EDTA)(OH); [Fe(EDTA)(OH)] = (3–6) × 10^{-4}M; pH = 10.5; Temp. = 25 °C; $\mu = 0.25$ M.

cyanide varying from one at high concentration to three at low cyanide concentration (Figure 1). This result points to stepwise displacement of EDTA by the cyanide ions. The overall stoichiometry of the reaction may be represented by Equation (1):

$$[\mathrm{Fe(EDTA)(OH)}]^{2-} + 5\,\mathrm{CN}^- \longrightarrow [\mathrm{Fe(CN)_5(OH)}]^{3-} + [\mathrm{EDTA}]^{4-} \qquad (1)$$

The absorption spectra of the solutions, after completion of the reaction, show a single peak at 395 nm due to formation of the $[\mathrm{Fe(CN)_5(OH)}]^{3-}$ ion⁽⁶⁾ as a product under the given experimental conditions. There is no evidence for the formation of $[\mathrm{Fe_2(CN)_{10}}]^{4-}$. The reverse reaction, *i.e.*, the reaction of EDTA with $\mathrm{Fe(CN)_5OH}$, using a large excess of EDTA, was found to be first order with respect to EDTA and $\mathrm{Fe(CN)_5(OH)}$; the reaction showed an inverse first order dependence in cyanide. These observations are compatible with the mechanism given in Equations (2–6) (charges have been omitted for sake of clarity):

$$\mathrm{FeY(OH)} + \mathrm{CN}^- \overset{K_1}{\rightleftharpoons} \mathrm{FeY(OH)(CN)} \qquad \text{(fast)} \quad (2)$$

$$\mathrm{FeY(OH)(CN)} + \mathrm{CN}^- \overset{K_2}{\rightleftharpoons} \mathrm{FeY(OH)(CN)_2} \qquad \text{(fast)} \quad (3)$$

$$\mathrm{FeY(OH)(CN)_2} + \mathrm{CN}^- \overset{K_3}{\rightleftharpoons} \mathrm{FeY(OH)(CN)_3} \qquad \text{(fast)} \quad (4)$$

$$\mathrm{FeY(OH)(CN)_3} + \mathrm{CN}^- \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} \mathrm{FeY(OH)(CN)_4} \qquad \text{(rds)} \quad (5)$$

$$\mathrm{FeY(OH)(CN)_4} + \mathrm{CN}^- \overset{K_5}{\rightleftharpoons} \mathrm{Fe(OH)(CN)_5} + \mathrm{Y}^{-4} \qquad \text{(fast)} \quad (6)$$

The inverse first order dependence in cyanide for the reverse reaction enables one to pinpoint the rate determining step as the fourth one (Equation 5). The variable order dependence in cyanide for the forward reaction, which changes from one to three, coupled with the above observation, leads to the proposition that the first step is very fast and the intermediate, FeY(OH)(CN), is formed instantaneously and is also sufficiently stable. Three cyanides react with this intermediate to produce $\mathrm{FeY(CN)_4(OH)}$ in the rate determining step, giving rise to the observed third order dependence in cyanide at low cyanide concentrations. However, as the concentration of cyanide increases, the reactants become $\mathrm{FeY(CN)_2(OH)}$ or $\mathrm{FeY(CN)_3(OH)}$, which accounts for the observed second and first order dependences respectively (Figure 1). A fourth order dependence can be observed when the reactant was FeY(OH) and not FeY(OH)CN as proposed above. We failed to see this because at still lower concentration of cyanide, where FeY(OH) may become a reactant, the reaction rate becomes too slow for dependable measurement. It may also be possible to see fourth order dependence in case of reaction of iron(III) complexes of other aminocarboxylates yet to be investigated. Whereas with nickel(II)⁽¹⁾ and cobalt(III)⁽²˒ ³⁾ reactions, three cyanides are required around the nickel or cobalt ions in the rate-determining step, in the present case four cyanides appear to encompass the iron(III) along with the remaining glycinate segment of EDTA and the hydroxyl group. The fifth cyanide adds very rapidly, displacing the remaining glycinate segment of EDTA and finally producing $\mathrm{Fe(CN)_5OH}$.

We intend studying the pH dependence and activation parameters of the forward and reverse reactions in order to throw further light on the proposed mechanism.

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