MeI

Small amounts of the dialkylated product (3; R,R' = alkyl) may be formed depending on reaction time and conditions. b.W. S. Ang and B. Halton, Aust. J. Chem., 1971, 24, 851. Apparent mixture of isomers, yield <2%. anthracyclinone synthesis.2 Addition of N-methylphthalimide in tetrahydrofuran (THF) to 2.1 equiv. of lithium metal in liquid NH3 at -78 °C gave a deep purple solution of the dianion (1b) which was characterized by reaction with various alkylating agents (Scheme).

The products isolated after quenching and work-up support the proposed dianion intermediate. The ratio of bridgehead to benzylic alkylation products (2): (3) appears to vary with the reactivity and steric bulk of the electro-While the products (2) resulted from regiospecific alkylation adjacent to the carbanion-stabilizing carbonyl groups of (1b), umpolung of the carbonyl centre, giving rise to the products (3), was the preferred pathway observed with the larger alkylating agents. Interestingly, no trace of the bridgehead alkylated product (2) was observed with allyl bromide. This result may in part be due to a facile enolate-Cope rearrangement3 following initial alkylation at the ring-fusion position. Silvlation of the dianion (1b) with a variety of reagents gave only the monosilylated product (3; R = H, $R' = SiMe_3$).

In conclusion, reduction of N-methylphthalimide occurs readily and cleanly to give the highly reactive and heretofore unknown dianion (1b). Application of this reaction as a method for preparing functionalized isoindoles and other heterocycles,4 as well as 1,3-dienes not easily accessible by alternative means, is being investigated.

(Received, 12th May 1980; Com. 504.)

¹ For a recent application of dissolving metal reduction of benzoic acid derivatives see: J. A. Marshall and P. G. M. Wuts, J. Org. Chem., 1977, 42, 1794.

² For application of isobenzofuran to anthracyclinone synthesis see: A. S. Kende, D. P. Curran, Y. Tsay, and J. E. Mills, Tetrahedron

Lett., 1977, 40, 3537.

Regeneration of the aromatic system could provide the driving force necessary to shift the equilibrium away from the commonly observed direction; D. A. Evans, D. J. Baillargeon, and J. W. Nelson, J. Am. Chem. Soc., 1978, 100, 2242.

Intermediates of type (3) have been utilized recently; V. Scartoni, R. Fiaschi, S. Catalano, I. Morelli, and A. Marsili, J. Chem. Soc.,

Detection of Paramagnetic Intermediates in the Reaction of Aqueous Titanium(III) Complexes with Dioxygen

By RICHARD CATTON, PAVLE PREMOVIC, LILLY STAVDAL, and PAUL WEST* (Department of Chemistry, University of Victoria, P.O. Box 1700, Victoria, British Columbia, Canada V8W 2Y2)

Summary At pH 7-9, the e.s.r. signal observed during reaction of aqueous titanium(III) tartrate complex with dioxygen is a singlet, g = 2.0134, assigned as the superoxide complex.

ACTIVATION of oxygen in haem model systems and in some oxidase enzymes involves electron transfer from a reducing metal ion, ultimately converting oxygen into water.1 Since the nature of the intermediate complexes of dioxygen, superoxide, and peroxide with the transition metal play a central role in these natural processes, it is important to consider model systems involving other one-electron reductants such as titanium(III). The overall process for such Fenton-like systems can involve attack on organic substrates (co-ordinating ligands) as shown schematically We have previously reported the in equations (1)—(3).

$$O_2 + Ti^{III} \rightarrow Ti^{IV} + (O_2 -) \xrightarrow{Ti^{IV}} Ti^{IV} + (O_2 -) \tag{1}$$

$$HOO^- + Ti^{III} \rightarrow OH^- + Ti^{IV} + O^-$$
 (2)

$$O^{-} + RH \rightarrow R^{\bullet} + OH^{-} \tag{3}$$

observation of radical ions (e.g. R.) when oxygen reacts with titanium(III) tartrate complexes at pH 12 using e.s.r. detection in a rapid flow system.2 Recently, using stopped flow spectrophotometry, rapid formation of a discrete peroxo titanium(IV) complex was observed on mixing [Ti(edta)(H2O)] with dioxygen at pH 4.573 (Hedta = ethylenediaminetetra-acetic acid).

We now report that 1 × 10-8M titanium(III) chloride complexed with an excess of tartaric acid (0.1 M) at pH 7.0 reacts with oxygenated water (ca. 1.0×10^{-8} M) in a rapid-flow e.s.r. system² to exhibit a relatively narrow singlet $\Delta H_{pp} = 0.16$ mT, 20—50 ms after mixing. A gvalue of 2.0134 ± 0.0002 is determined relative to the tartrate ketyl trianion $-O_2CC(O^-)CHOHCO_2^-$, g=2.0042 with a_{CHOH} (1) 0.266 mT. The latter species can be generated under virtually identical spectrometer conditions by allowing the titanium(III) solution to react with basic 0.0125 м hydrogen peroxide solution instead of oxygenated water in a consecutive experiment. The same mixing cell-cavity configuration is maintained throughout the sequence.

When the initial titanium(III) tartrate solution is adjusted to pH 9.0-9.5, a less intense second singlet appears at g = 2.0145. Its intensity is sharply increased when metal ion solutions are deliberately partially hydrolysed, indicating probable dimeric complexes containing superoxide ligands. The first singlet is still 3 times more intense at pH 9.0.

In order to assign the signal at g = 2.0134 to a titanium-(III) dioxygen complex, it is necessary to eliminate possible peroxyl radicals ROO. that would arise through capture of the ketyl in a full 'Fenton' sequence, equation (4).

$$R \cdot + O_2 \longrightarrow RO_2 \cdot + OH^-$$
 (4)

During our initial work2 we measured peroxide yields for the reaction of 2 × 10⁻³ m titanium(III) tartrate with 1 × 10⁻³ m oxygenated water over the pH range 8-12, obtaining a conversion of oxygen into peroxide of 75% at pH 9.0. In these experiments we acidified after mixing and assayed the peroxo titanium(IV) complex at pH 0.8 (\lambda_{max} 405 nm, € 830). In agreement with Kristine and Shepherd³ we observed promptly the yellow peroxo titanium(IV) tartrate complex (\lambda_max 348 nm) at pH 8-10.5. Clearly, in the light of these studies on two electron reduction, it is kinetically unlikely that the g = 2.0134 signal is due to an alkylperoxyl species. Such peroxyl radicals, in any event, normally give broad signals at giso values of 2.0150-

In further experiments we have allowed titanium(III) to form a complex with sodium gluconate at pH 7.0-9.0, observing an analogous singlet at g = 2.0128 on reaction with 1 equiv. of oxygen. Now the g value is relative to the gluconate 2-ketyl radical (HOCH₂)(CHOH)₈ C(O⁻)CO₂, g = 2.0042, $a_{CHOH}(1) 0.66 \text{ mT.}^5$ Attempts to generate the Ti(edta)O, species by flowing aqueous dioxygen against 1 mm Ti(edta)H₂O- gave no signal over the pH range 4-9.

Comparison of the observed g values (2.0134, 2.0128) with approximate gav. values derived from data on anisotropic superoxide complexes in the solid state6 lends support to the assignment of the signals to titanium(III) dioxygen complexes.

The authors thank the National Science and Engineering Research Council of Canada for financial support.

(Received, 9th June 1980; Com. 619.)

⁶B. R. McGarvey and E. L. Tepper, Inorg. Chem., 1969, 8, 498; Y. Chimura, M. Beppu, S. Yoshida, and K. Tomara, Bull. Chem. Soc., Japan, 1977, 50, 691; J. Latour, J. Marchon, and M. Nakajima, J. Am. Chem. Soc., 1979, 101, 3974.

Co-ordination Polymers of Rhodium(1+) with Di-isocyanonaphthalene (1,4 and 1,5) Linkages

By Avi Efraty,* Irene Feinstein, Felix Frolow, and Alexander Goldman (Departments of Organic Chemistry and Structural Chemistry, The Weizmann Institute of Science, Rehovot, Israel)

Summary The template polymerization of tetragonal rhodium(1+) with 1,4- and 1,5-di-isocyanonaphthalenes gives two-dimensional co-ordination polymers with a stacked layers arrangement; the powder X-ray diffractometric traces of these polymers are presented and discussed.

THE isomers 1,4- and 1,5-di-isocyanonaphthalene1 can be regarded as non-chelating bidentate ligands capable of forming stereochemically rigid linkages between metal nuclei with a bridge span of ca. 12 Å. Viewing the terminal isocyanide-to-metal bonds as vectors suggests that the terms 'colinear' (1,4) and 'parallel' (1,5) may be used to describe the bridging geometries of these ligands. Compared with the colinear (1,4) ligand, a displacement of 2.42 Å between the parallel vectors in 1,5-di-isocyanonaphthalene requires a slightly longer bridge span (ca. 0.2 Å). The co-ordination properties of these bridging ligands were ascertained for a tetragonal rhodium(1+) system.

Di-isocyanonapthalenes (1,4 and 1,5) react with [Rh-(CO)2Cl]2 in CH2Cl2 solution to afford quantitative yields of insoluble green polycrystalline polymers which analyse as [Rh(bridge)2+Cl-]n. These polymers readily absorb water, and therefore, unless rigorously dried in vacuo, are best formulated as $[Rh(bridge)_2+Cl-xH_2O]_n$ (x=0-5). A single strong v(NC) at 2040 ± 5 cm⁻¹ in their i.r. spectra may suggest the presence of terminally co-ordinated isocyanides in a symmetric environment.

Two-dimensional models of the [Rh(bridge)2]n network which depict the template polymerization of tetragonal RhI with 1,4-di-isocyanonaphthalene [Figure (A)] and