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Reactions of Dinitrogen Oxide (Nitrous Oxide) with Dicyclopentadienyltitanium Complexes Including a Reaction in Which Carbon Monoxide Is Oxidized

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Abstract: Dinitrogen oxide (N_2O) oxidized $(Cp_2TiCl)_2$ (Cp = η^5-C_5H_5) to $(Cp_2TiCl)_2O$ according to the equation $(Cp_2TiCl)_2 + N_2O \rightarrow (Cp_2TiCl)_2O + N_2$. N_2O rapidly reacted with a toluene solution of Cp_2Ti at 0 °C to form the new Ti(III) complex $(Cp_2Ti)_2O$ according to the equation $2Cp_2Ti + N_2O \rightarrow (Cp_2Ti)_2O + N_2$. $(Cp_2Ti)_2O$ was very reactive: with CO_2 at 20 °C in toluene it gave $[(Cp_2Ti)_4(CO_3)_2]$ within minutes; it was oxidized by excess N_2O to a Ti(IV) polymer; with CO it gave a mixture of $Cp_2Ti(CO)_2$, the Ti(IV) polymer, and a CO_2 complex, believed to be $(Cp_2Ti)_2(CO_2)$. At 65 °C in toluene N_2O reacted with an excess of $Cp_2Ti(CO)_2$ over 12 h according to the equation $4Cp_2Ti(CO)_2 + 4N_2O \rightarrow [(Cp_2Ti)_4(CO_3)_2] + 4N_2 + 6CO$. $[(Cp_2Ti)_4(CO_3)_2]$ was oxidized by excess N_2O according to the equation $[(Cp_2Ti)_4(CO_3)_2] + 2N_2O \rightarrow$ Ti(IV) polymer $+ 2CO_2 + 2N_2$. Dioxygen (O_2) reacted quantitatively with $Cp_2Ti(CO)_2$ to give $[(Cp_2Ti)_4(CO_3)_2]$ according to the equation $4Cp_2Ti(CO)_2 + 2O_2 \rightarrow [(Cp_2Ti)_4(CO_3)_2] + 6CO$. Mechanistic studies indicate that the CO oxidation reactions proceed via initial insertion of an oxygen atom of O_2 or N_2O into the Ti–C bond. Physical properties of $(Cp_2Ti)_2O$, $[(Cp_2Ti)_4(CO_3)_2]$, and the blue dimeric complex $[(Cp_2Ti)_2(CO_3)]$ (into which $[(Cp_2Ti)_4(CO_3)_2]$ dissociates in solution) are reported.

Introduction

Dinitrogen oxide (nitrous oxide) is an interesting inorganic reagent whose behavior toward transition-metal complexes has been little investigated. Potentially N_2O, which is isoelectronic with NCO^-, might be expected to act as an unidentate ligand, bonding either through nitrogen (with an essentially linear MNNO group) or through oxygen (with a bent MONN group); a further possibility is bidentate N_2O, bonding through N and O. To date only one complex containing N_2O has been definitively characterized, that being $[Ru(NH_3)_5(N_2O)]^{2+}$,[2,3] and this has been shown to be N bonded.[4] In this complex the N_2O is very readily replaced by other ligands. The existence of the dimeric, presumably N,O bonded $[(Ru(NH_3)_5)_2(N_2O)]^{4+}$ has also been suggested.[5] A purposeful attempt to prepare an N_2O complex of iridium(III) showed that the N_2O ligand was extremely rapidly replaced by the solvent H_2O, and no N_2O complex could be isolated.[6] The small amount of evidence available suggests therefore that N_2O is a very poor ligand.

It might also be expected that N_2O would act as a mild oxidizing agent toward transition-metal complexes. This aspect has been briefly explored;[7,8] the catalytic oxidation of Ph_3P to Ph_3PO by N_2O using $[(Ph_3P)_3Co(H)N_2]$ as catalyst[7] was interesting to us in that it indicated that ligand rather than metal oxidation by N_2O was possible. The mild oxidation of ligands, particularly of carbon monoxide, is a topic of current importance.[9] We finally note that N_2O is also isoelectronic with CO_2, and as with CO_2 there is an expanding literature of the reactions of N_2O on transition-metal surfaces.[10] The surface reactions of CO_2 have recently been extended to homogeneous solutions of transition-metal complexes,[11-14] and some of these CO_2 reactions are related to those of N_2O described here.

In order to investigate the potential of N_2O for mild oxidation, and to continue our search for N_2O complexes, we have begun a thorough investigation of the reactions of N_2O with transition-metal complexes. We present here the results of a study of the reactions between N_2O and derivatives of Cp_2Ti (Cp = η^5-cyclopentadienyl, η^5-C_5H_5). A brief report of part of this work has appeared.[15]

Results and Discussion

Reaction of N_2O with Titanium(III) Complexes. Dinitrogen oxide reacted slowly with the titanium(III) complex $(Cp_2TiCl)_2$[16] in tetrahydrofuran solution at room temperature, giving the orange titanium(IV) dimer $(Cp_2TiCl)_2O$,[17] according to the equation[18]

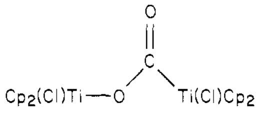
$$(Cp_2TiCl)_2 + N_2O \rightarrow (Cp_2TiCl)_2O + N_2 \qquad (1)$$

The reaction proceeded more rapidly in toluene at 65 °C, but even then millimolar quantities required 6 h for complete reaction.

Floriani and co-workers observed a related reaction between $(Cp_2TiCl)_2$ and CO_2[14]

$$(Cp_2TiCl)_2 + CO_2 \rightarrow (Cp_2TiCl)_2O + CO \qquad (2)$$

and proposed that the reaction proceeded via an intermediate:



Because of the strength of the N≡N bond and the different

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[18] As described in the Experimental Section, the stoichiometries of all reactions described were totally determined, using Toepler pump techniques for the gaseous reactants and products. Orthodox weighing was used to determine solid product ratios. Because of the difficulties in separating and handling the extremely air-unstable products their ratios are less accurate. Where the yellow Ti(IV) polymer was a solid product its quantity could only be determined by difference.

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electronegativities of N and O, the canonical form $N{\equiv}N^+{-}O^-$ will make a much larger contribution to the structure of N_2O than $O^+{\equiv}C{-}O^-$ makes to CO_2, and therefore an intermediate of the type proposed by Floriani is much less likely in the reaction between N_2O and $(Cp_2TiCl)_2$. It seems more probable that the initial reaction is electrophilic cleavage of the $(Cp_2TiCl)_2$ dimer by the oxygen atom of N_2O. This would account for the slowness of the reaction, since the single O atom must obtain one electron from a "d_{y^2}" orbital on each Ti[19] (the Ti–Ti distance in $(Cp_2TiCl)_2$ is 3.95 Å[20]) and considerable electronic rearrangement is necessary. In contrast oxidation by the diradical O_2 (O–O 1.21 Å[21]) is rapid. It is also possible that the difference in the rate of oxidation by O_2 compared to N_2O indicates that a radical mechanism of oxidation is occurring.

Dinitrogen oxide oxidized the titanium(III) complexes $[(Cp_2Ti)_4(CO_3)_2]$ and $(Cp_2Ti)_2O$ (see below) according to the equations

$$(Cp_2Ti)_2O + N_2O \rightarrow 2\text{“}Cp_2TiO\text{”} + N_2 \qquad (3)^{22}$$

$$[(Cp_2Ti)_4(CO_3)_2] + 2N_2O \rightarrow 4\text{“}Cp_2TiO\text{”} + 2CO_2 + 2N_2 \qquad (4)^{22}$$

The loss of CO_2 on oxidation of $[(Cp_2Ti)_4(CO_3)_2]$ was surprising, and indicated a rather complicated redox reaction. In general, however, N_2O appeared to be a mild, clean oxidizing agent toward Ti(III).

Reaction of N_2O with Cp_2Ti^{II}. Formation and Properties of $(Cp_2Ti)_2O$. When N_2O was admitted into the green-black toluene solution of Cp_2Ti[24,25] at 0 °C, there was instantaneous uptake of N_2O with formation of a blue solution. Almost immediately the solution began to froth and turned green-brown. Removal of excess N_2O and addition of hexane after 5 min[26] reaction time gave a khaki-green precipitate of $(Cp_2Ti)_2O$. The reaction stoichiometry was[27]

$$2Cp_2Ti + N_2O \rightarrow (Cp_2Ti)_2O + N_2 \qquad (5)$$

$(Cp_2Ti)_2O$ was characterized by microanalysis, mass, ESR, and IR spectra, and reactivity.

$(Cp_2Ti)_2O$ was very soluble in toluene, and the toluene solutions were extremely reactive.[28] With CO_2 the solution became green within 30 min and an essentially quantitative yield of $[(Cp_2Ti)_4(CO_3)_2]$ was obtained. The ESR spectrum of the $(Cp_2Ti)_2O/CO_2$ solution showed almost instantaneous disappearance of the $(Cp_2Ti)_2O$ signal at $g = 1.975$ and appearance of a signal at $g = 1.978$, assigned to $[(Cp_2Ti)_2(CO_3)]$ (see below). The reaction can be represented by the equation

$$2(Cp_2Ti)_2O + 2CO_2 \rightarrow [(Cp_2Ti)_4(CO_3)_2] \qquad (6)$$

With N_2O there was oxidation of $(Cp_2Ti)_2O$ (eq 3). In the presence of a large excess of CO a disproportionation reaction was observed

$$(Cp_2Ti)_2O + 2CO \rightarrow \text{“}Cp_2TiO\text{”} + Cp_2Ti(CO)_2 \qquad (7)^{22}$$

The reaction is, however, more complicated and interesting than implied by the simple reaction 7. If a 1:1 stoichiometric amount of CO was added to $(Cp_2Ti)_2O$ in toluene, the infrared spectrum of the solution showed absorptions at 1360 and 1440 cm^{-1}, as well as carbonyl bands due to $Cp_2Ti(CO)_2$. Attempts to isolate the new species were unsuccessful, a mixture of $(Cp_2Ti)_2O$, $Cp_2Ti(CO)_2$, and "Cp_2TiO"[22] being obtained, although the crude product did show IR bands at 1360 and 1440 cm^{-1}. The most reasonable explanation of the results is the equilibrium

$$(Cp_2Ti)_2O + CO \rightleftharpoons (Cp_2Ti)_2(CO_2) \qquad (8)$$

Note that addition of CO to $(Cp_2Ti)_2O$ did not result in CO_2 appearing in the gas phase, and that similar IR bands were observed in the reaction between Cp_2Ti and CO_2 (see below).

Reaction of N_2O with $Cp_2Ti(CO)_2$. At 65 °C N_2O reacted with an excess of $Cp_2Ti(CO)_2$ in toluene solution over a period of 6–12 h according to the equation

$$4Cp_2Ti(CO)_2 + 4N_2O \rightarrow [(Cp_2Ti)_4(CO_3)_2] + 4N_2 + 6CO \qquad (9)$$

Under the conditions described no other gaseous or titanium-containing products could be isolated. Excess $Cp_2Ti(CO)_2$ reacted with O_2 in a reaction very similar to (9)

$$4Cp_2Ti(CO)_2 + 2O_2 \rightarrow [(Cp_2Ti)_4(CO_3)_2] + 6CO \qquad (10)$$

and Floriani and co-workers have demonstrated a related reaction between $Cp_2Ti(CO)_2$ and excess CO_2

$$4Cp_2Ti(CO)_2 + 4CO_2 \rightarrow [(Cp_2Ti)_4(CO_3)_2] + 10CO \qquad (11)$$

Mechanism of Formation of $[(Cp_2Ti)_4(CO_3)_2]$ from Cp_2Ti Derivatives. We have made a preliminary investigation of the mechanism of reaction 9. It should be noted first that, when $Cp_2Ti(CO)_2$ reacted with an excess of N_2O (in either a static system or on passing N_2O through the solution), "Cp_2TiO"[22] and not $[(Cp_2Ti)_4(CO_3)_2]$ was obtained. The reaction stoichiometry approximated to the sum of reactions 9 (formation of $[(Cp_2Ti)_4(CO_3)_2]$) and 4 (oxidation of $[(Cp_2Ti)_4(CO_3)_2]$ by N_2O)

$$2Cp_2Ti(CO)_2 + 3N_2O \rightarrow 2\text{“}Cp_2TiO\text{”} + 3N_2 + 3CO + CO_2 \qquad (12)^{22}$$

in that the N_2O:N_2:CO ratio was 1.10:1:1.14 (mean of five experiments). However, a low yield of CO_2 (~15% of the amount of CO or N_2 produced instead of the expected 33%) was observed. Even when $Cp_2Ti(CO)_2$ was in excess, a small amount of yellow, presumably Ti(IV), material formed initially on the surface of the solution. This redissolved as the reaction proceeded.

When the reaction between N_2O and excess $Cp_2Ti(CO)_2$ was conducted at 20 °C, formation of $[(Cp_2Ti)_4(CO_3)_2]$ was very slow, but appeared to be complete in about 7 days for millimolar quantities. After a reaction time of 0.5 h at 20 °C a small quantity of brown material precipitated, which mainly redissolved as the reaction proceeded; however, unlike the reaction at 65 °C, some brown material was also obtained at the end of the reaction in addition to $[(Cp_2Ti)_4(CO_3)_2]$. The brown material had very similar chemical and physical properties to the material obtained when Cp_2Ti and N_2O were allowed to react for periods longer than 5 min;[26] i.e., the material is derived from $(Cp_2Ti)_2O$.

Gas sampling during reaction revealed that the N_2O:N_2:CO ratio during the early stages of the reaction was close to 1:1:1, changing to 2:2:3 (as required by reaction 10) during reaction. Traces of free CO_2 were observed during the reaction. The IR spectrum of the reaction solution at 20 °C showed broadening of the ν(CO) absorptions in the 1900-cm^{-1} region, indicating the presence of metal carbonyl species other than $Cp_2Ti(CO)_2$. The

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[22] The nature of the yellow product obtained on oxidation of derivatives of Cp_2Ti has been the subject of some discussion.[17,23] There is general agreement that the product is a polymer containing Ti(IV). The material obtained by us had analyses appropriate to formulas ranging from Cp_4TiO_2 to Cp_2TiO_2, depending on the reaction concerned. The gas-phase stoichiometry indicated oxygen appropriate to the formula Cp_2TiO (except when very large excesses of oxidizing agent were used). This formula is therefore used in the text.

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[25] Bercaw, J. E.; Marvich, R. H.; Bell, L. G.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1972**, *94*, 1219.

[26] When the reaction between Cp_2Ti and N_2O was allowed to proceed for longer than 5 min, the pyrophoric brown material obtained was much less soluble in toluene than $(Cp_2Ti)_2O$, showed a signal at $g = 1.979$ in the ESR spectrum ($(Cp_2Ti)_2O$ showed only the $g = 1.975$ signal) and gave variable microanalytical results (C, 52.7–56.3; H, 4.8–5.2). Oxidation of $(Cp_2Ti)_2O$ by N_2O was independently observed (see text, eq 3), but the product was the insoluble, diamagnetic Ti(IV) polymer. The precise nature of the material obtained over longer reaction times is still uncertain.

[27] The amount of Cp_2Ti in solution was determined by its reaction with N_2 at −78 °C (see Experimental Section and ref 24 and 25).

[28] $(Cp_2Ti)_2O$ dissolved in toluene to give an initially brown solution. On setting these solutions aside the color changed over a period of hours, becoming eventually blue. The ESR spectrum of the blue solutions showed only very weak signals in the $g = 1.979$ region. The same blue material can apparently be obtained by heating $[(Cp_2Ti)_4(CO_3)_2]$ (see text). The reactions described were performed on freshly prepared solutions of $(Cp_2Ti)_2O$.

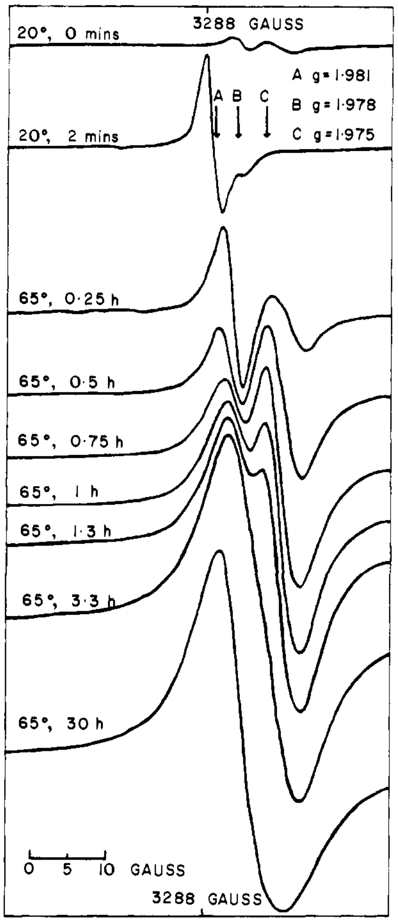
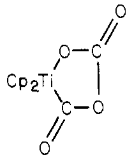


Figure 1. Electron spin resonance spectra of the reaction between N_2O and $Cp_2Ti(CO)_2$ in toluene solution. The uppermost spectrum is of $Cp_2Ti(CO)_2$ in toluene solution under vacuum. The second spectrum is from the reaction at 20 °C. Subsequent spectra are of the reaction at 65 °C. Signal A is assigned to an adduct between $Cp_2Ti(CO)_2$ and N_2O (see text); signal B is assigned to $(Cp_2Ti)_2CO_2$; signal C is assigned to $(Cp_2Ti)_2O$.

spectrum also showed weak absorptions in the 1600- and 1400-cm^{-1} region, probably indicative of a CO_2 species.

The ESR spectrum of $Cp_2Ti(CO)_2$ at 20 °C always showed very weak signals at $g = 1.978$ and 1.975 due to the unavoidable presence of oxidized impurity. On adding N_2O there was immediate appearance of a strong signal at $g = 1.981$, followed with 60 s by appearance of a second signal at $g = 1.978$. If the N_2O reactant was pumped off, the $g = 1.981$ signal disappeared, leaving only the $g = 1.978$. On readmitting N_2O, the $g = 1.981$ signal reappeared. After about 5 min a third signal at $g = 1.975$ appeared. As the reaction proceeded all three signals became extremely broad owing to formation of insoluble $[(Cp_2Ti)_4(CO_3)_2]$, the spectrum of which, in saturated solution, showed only a very broad band centered at $g = 1.980$. If N_2O and excess $Cp_2Ti(CO)_2$ were allowed to react at 20 °C for 30 min and the gaseous reactants and products pumped off, the remaining solution did not give $[(Cp_2Ti)_4(CO_3)_2]$, but on admitting CO_2 this product was obtained much more rapidly than could be explained by formation of $[(Cp_2Ti)_4(CO_3)_2]$ from $Cp_2Ti(CO)_2$ and CO_2. Readdition of N_2O only gave $[(Cp_2Ti)_4(CO_3)_2]$ at the rate which would be expected if N_2O was reacting with residual $Cp_2Ti(CO)_2$.

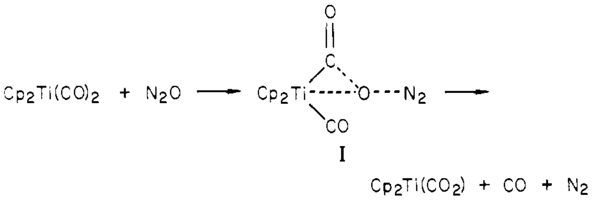
The ESR spectrum of the reaction at 65 °C did not show the initial signal at $g = 1.981$. Only the $g = 1.978$ and 1.975 signals appeared, increasing in intensity and broadening with time as before. The spectra observed are illustrated in Figure 1. The ESR spectra of the reaction between O_2 and $Cp_2Ti(CO)_2$ were similar to those of the N_2O reaction, except that at 20 °C only an extremely weak signal at $g = 1.975$ appeared.



Floriani et al. have suggested that in the reaction between $Cp_2Ti(CO)_2$ and excess CO_2 the (formally Ti(IV)) intermediate was formed.[14] This was then reduced by $Cp_2Ti(CO)_2$ to $[(Cp_2Ti)_4(CO_3)_2]$. In conformity with this proposal we found that the ESR spectrum of the reaction between $Cp_2Ti(CO)_2$ and CO_2 at 20 or 65 °C showed only the very weak signals at $g = 1.978$ and 1.975 observed for $Cp_2Ti(CO)_2$ itself. No other signals were observed until, after several hours, the broad peak of $[(Cp_2Ti)_4(CO_3)_2]$ appeared. During the reaction between $Cp_2Ti(CO)_2$ and CO_2 at 20 °C no brown material of the type seen in the reaction between $Cp_2Ti(CO)_2$ and N_2O was observed; only the $[(Cp_2Ti)_4(CO_3)_2]$ product precipitated.

Toluene solutions of Cp_2Ti absorbed excess CO_2 at 20 °C giving $[(Cp_2Ti)_4(CO_3)_2]$ in 40% yield after 72 h reaction time. The ESR spectrum of the reaction solution showed a single intense unsymmetrical peak at $g = 1.978$, which was present within 5 min of commencement of reaction. This signal was obliterated by the strong symmetrical signal due to $[(Cp_2Ti)_4(CO_3)_2]$, also at $g = 1.978$, during the course of the reaction. When CO_2 was reacted with excess Cp_2Ti, or short reaction times for the reaction between excess Cp_2Ti and CO_2 were used, $[(Cp_2Ti)_4(CO_3)_2]$ was not observed. The infrared spectrum of the reaction solution showed the same absorptions at 1360 and 1440 cm^{-1} as were observed in the reaction between $(Cp_2Ti)_2O$ and CO (see above). We therefore conclude that the same CO_2 complex, $(Cp_2Ti)_2(CO_2)$, was being formed.

The results allow at least the basic mechanism of reactions 9 and 10 to be outlined. As has been previously suggested for reactions of $Cp_2Ti(CO)_2$, the first step must be bimolecular attack of N_2O giving a transient species (I), to which we assign the ESR signal at $g = 1.981$ and which rapidly converts to a diamagnetic $Cp_2Ti(CO_2)$ complex, in a similar manner to the formation of $[Cp_2Ti(COMe)Cl]$.[29]



$$Cp_2Ti(CO)_2 + N_2O \longrightarrow Cp_2Ti(CO)(\cdots O \cdots N_2)(C{=}O)\ (\mathrm{I}) \longrightarrow Cp_2Ti(CO_2) + CO + N_2 \qquad (13)$$

The most reasonable sequence of subsequent reactions which lead to $[(Cp_2Ti)_4(CO_3)_2]$ and which is consistent with all the observations is

$$2Cp_2Ti(CO_2) \rightarrow (Cp_2Ti)_2(CO_2) + CO_2 \qquad (14)$$

$$(Cp_2Ti)_2(CO_2) \rightleftharpoons (Cp_2Ti)_2O + CO \qquad (15)$$

$$(Cp_2Ti)_2O + CO_2 \rightarrow {}^1/_2[(Cp_2Ti)_4(CO_3)_2] \qquad (16)$$

The ESR signal at $g = 1.978$ is assigned to $(Cp_2Ti)_2(CO_2)$, and that at $g = 1.975$ to $(Cp_2Ti)_2O$ (see above). Reactions 15 and 16 have been discussed above. The observation of only traces of CO_2 in the gas phase, and the known rapidity of reaction 16, indicates that the slow step is dimerization reaction 14.

The proposed mechanism also accommodates some local oxidation of $Cp_2Ti(CO)_2$ to Ti(IV) by N_2O, if it is assumed that the Ti(IV) product can be reduced to $(Cp_2Ti)_2O$ by $Cp_2Ti(CO)_2$. A related reduction, that of Cp_2TiCl_2 to $(Cp_2TiCl)_2$ by $Cp_2Ti(CO)_2$, has been observed previously.[30]

A similar mechanism to that given in eq 13–16 can be proposed for the reaction between O_2 and $Cp_2Ti(CO)_2$, with O_2 oxidizing

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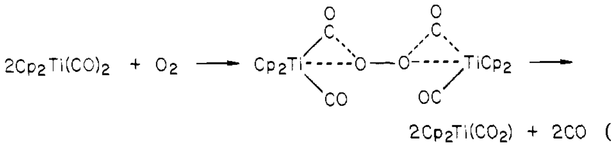
[29] Fachinetti, G.; Floriani, C.; Stoeckli-Evans, H. *J. Chem. Soc., Dalton Trans.* **1977**, 2297.

[30] Floriani, C.; Fachinetti, G. *J. Chem. Soc., Dalton Trans.* **1973**, 1954.

two molecules of $Cp_2Ti(CO)_2$ either simultaneously ($Cp_2Ti(CO)_2$ being in excess) or in a two-step reaction equivalent to eq 13



(17)

The sequence in eq 14–16 follows as in the N_2O reaction.

Properties of $[(Cp_2Ti)_4(CO_3)_2]$. The complex $[(Cp_2Ti)_4(CO_3)_2]$ was obtained from a number of reactions described in this work. It is therefore necessary to describe its properties in some detail.

As a Fluorolube mull $[(Cp_2Ti)_4(CO_3)_2]$ was green and showed IR absorptions at 1475 (m) and 1425 (s) cm^{-1}, assignable to CO_3^{2-}. In a freshly prepared solution it was also green and showed a strong signal at $g = 1.980$ and a very weak signal at $g = 1.978$ in the ESR spectrum. The solution became blue with time, and the $g = 1.980$ signal decreased in intensity, the $g = 1.978$ increasing until after 6 h only the latter was observable. Whereas the green solid $[(Cp_2Ti)_4(CO_3)_2]$ showed no half-field line at −196 °C, the blue solution showed such a line. The green to blue transformation proceeded more easily in THF than in toluene, and in this solvent the complex showed IR absorptions at 1580 and 1355 cm^{-1}, but none at 1475 or 1425 cm^{-1}. The molecular weight in THF (by osmometry) was 435. However, on cooling the toluene solutions, or on evaporating either THF or toluene off and drying, green $[(Cp_2Ti)_4(CO_3)_2]$ was reobtained essentially quantitatively. We propose that the solutions contain the dimeric steel-blue $[(Cp_2Ti)_2(CO_3)]$ ($M = 416.2$) in equilibrium with light-green $[(Cp_2Ti)_4(CO_3)_2]$

$$[(Cp_2Ti)_4(CO_3)]_2 \rightleftarrows 2[(Cp_2Ti)_2(CO_3)] \qquad (18)$$

Coutts and Wailes have in fact described a blue paramagnetic $[(Cp_2Ti)_2(CO_3)]$ complex having IR absorptions (KBr pellet) at 1530 and 1355 cm^{-1}, which they obtained from the reaction between CO_3^{2-} and aqueous solutions of $[Cp_2Ti]^+$.[31] However, our attempts to repeat this showed that the blue material always contained solvent. On removal of solvent under vacuum green $[(Cp_2Ti)_4(CO_3)_2]$ was once again obtained. The lack of a half-field ESR signal for $[(Cp_2Ti)_4(CO_3)_2]$ agrees with its normal magnetic moment,[14] and the presence of such a signal for $[(Cp_2Ti)_2(CO_3)]$ agrees with its low moment.[31]

The ESR spectrum of $[(Cp_2Ti)_4(CO_3)_2]$ is noteworthy in that only a single-line spectrum at 20 °C was observed. In the structure of $[(Cp_2Ti)_4(CO_3)_2]$ there are two differently coordinated pairs of titanium ions;[14] hence two signals at room temperature could be expected. Two possible explanations for the single-line spectrum are worth considering: firstly, that there is fast exchange between the Ti coordination sites (this is unlikely in the solid state, and even in solution exchange is slow, as shown by the simultaneous presence of signals due to $[(Cp_2Ti)_4(CO_3)_2]$ and $[(Cp_2Ti)_2(CO_3)]$; secondly, that there is insufficient difference in the environment at Ti to produce two signals. In the solid state both Ti atoms are coordinated by two oxygens, one with Ti–O = 2.183 Å and O–Ti–O = 69.1° and the other with Ti–O = 2.128 Å and O–Ti–O = 61.3°. The environments are therefore sufficiently similar to be undetected by ESR given the line width in this type of complex.

On refluxing for several days the steel-blue toluene solutions of $[(Cp_2Ti)_2(CO_3)]$ became royal blue, and on cooling a royal blue precipitate was obtained, along with unreacted green $[(Cp_2Ti)_4(CO_3)_2]$, which could be removed by dissolution in ether. The same result was obtained when $[(Cp_2Ti)_4(CO_3)_2]$ was heated in vacuo. Neither CO nor CO_2 was evolved on heating in vacuo. The steel-blue product showed very weak ESR signals in the $g = 1.978$ region and no features other than those attributable to Cp in the infrared spectrum. Microanalysis indicated a Cp:Ti ratio of 1:1. We believe that this complex is the same as, or related to, the $Cp_6Ti_6O_8$ cluster previously described by Caulton and co-workers,[32] but, because we have been unable to obtain reproducible chemical and physical properties, we have not pursued this investigation. A similar complex apparently could be obtained from $(Cp_2Ti)_2O$.[28]

Experimental Section

All compounds described were extremely air sensitive. Standard vacuum line, Schlenck-ware, and drybox or glovebag techniques were used in the handling of the reactions and their products. Diethyl ether, tetrahydrofuran, hexane, and toluene were stored over methyllithium under vacuum and distilled under vacuum. Dicyclopentadienyltitanium dichloride (Cp_2TiCl_2) was obtained from Strem Chemicals. Argon, used as blanketing gas, was 99.996%. Dinitrogen oxide was 99%. Bis(dicyclopentadienyltitanium chloride) ($(Cp_2TiCl)_2$)[16] and dicyclopentadienyltitanium dicarbonyl ($Cp_2Ti(CO)_2$)[33] were prepared by the literature methods. Toluene solutions of dicyclopentadienyltitanium (Cp_2Ti) were obtained from Cp_2TiCl_2 via the intermediates $Cp_2Ti(CH_3)_2$ and $(Cp_2TiH)_x$ as previously described.[24,25,34]

Reaction of Dinitrogen Oxide with Bis(dicyclopentadienyltitanium chloride). Bis(dicyclopentadienyltitanium chloride) Oxide ($(Cp_2TiCl)_2O$). In a typical experiment $(Cp_2TiCl)_2$ (0.15 g, 0.35 mmol) was dissolved in THF (25 cm^3) and stirred for 48 h at 20 °C under N_2O (0.94 mmol, measured by means of a bulb of known volume (~100 cm^3) and a manometer). The solution slowly changed color from green to orange. The gases were then Toeplered, the first fraction being obtained after trapping with liquid nitrogen, the second using 2-propanol/solid CO_2 traps (−78 °C). The first fraction was 0.75 mmol, the second 0.25 mmol. The infrared spectrum of the second fraction showed N_2O and a small amount of THF. Hexane (~50 cm^3) was added to the orange solution which remained, the mixture was allowed to stand overnight, and the orange crystals of $(Cp_2TiCl)_2O$ which precipitated were removed by filtration, yield 0.12 g (77%). Anal. Calcd for $C_{20}H_{20}Cl_2Ti_2O$: C, 54.2; H, 4.55; Cl, 16.0. Found: C, 54.2; H, 4.7; Cl, 16.0. NMR: singlet in acetone-d_6 at τ 3.55 (lit. 3.65).[17] IR: 3080 s, br; 1060, 1045 w; 1005; 1000; 990 m; 850; 830 m; 810, 790, 780 s; 720 s, br cm^{-1}. From an average of five such experiments the reaction stoichiometry $1(Cp_2TiCl)_2 + 1N_2O \rightarrow 0.85\ (\pm 0.3)(Cp_2TiCl)_2O + 1.2(\pm 0.4)N_2$ was established.

Reaction of Dinitrogen Oxide with Dicyclopentadienyltitanium. Bis(dicyclopentadienyltitanium) Oxide ($(Cp_2Ti)_2O$). In a typical experiment to determine the reaction stoichiometry toluene (20 cm^3) was distilled onto $(Cp_2TiH)_x$[25] (0.25 g) and the mixture stirred for 2 h at 20 °C, the evolved H_2 being occasionally pumped away. The resultant dark green solution was cooled to −78 °C and N_2 added, giving an immediate intensely blue color. The excess N_2 was pumped away, the solution warmed to room temperature, and the evolved N_2 Toeplered. Assuming that the stoichiometry of the N_2 complex was $[(Cp_2Ti)_2(N_2)]$,[24,25] this procedure showed that the amount of Cp_2Ti in solution was 1.2 mM. The solution was cooled in an ice bath and N_2O (1.5 mM) added. After frothing had subsided the resultant green-brown mixture was stirred for 5 min at 0 °C, then the gases were Toeplered, first through liquid-nitrogen traps (evolved N_2 = 0.67 mmol), then through 2-propanol/solid CO_2 traps (residual N_2O = 0.74 mmol; purity checked by IR spectroscopy). An average of four such experiments established the reaction stoichiometry as $2Cp_2Ti + 1N_2O \rightarrow 0.8(\pm 0.2)(Cp_2Ti)_2O + 1.1(\pm 0.2)N_2$.

To obtain a pure solid sample of $(Cp_2Ti)_2O$, $(Cp_2TiH)_x$ (1.1 g) was stirred at 20 °C in toluene for 2 h, the evolved H_2 being occasionally pumped away. The solution was cooled to 0 °C, N_2O (>10 mmol) added, and the mixture stirred for 5 min. The N_2O/N_2 gas mixture was then pumped away, the mixture filtered, and to the filtrate hexane (40 cm^3) added. After standing for 15 min the khaki-green $(Cp_2Ti)_2O$ was filtered off, washed with hexane, and vacuum dried, yield 0.25 g (22%).

Caution: When dry, $(Cp_2Ti)_2O$ was explosively oxidized by air. Appropriate precautions should be taken when removing apparatus from the line; it is not recommended that large quantities of this material be prepared.

Anal. Calcd for $C_{20}H_{20}Ti_2O$: C, 64.5; H, 5.4; Ti, 25.8. Found: C, 64.2; H, 5.2; Ti (as TiO_2), 26.0. The mass spectrum showed peaks at m/e 372, 307, and 178, corresponding to $(Cp_2Ti)_2O^+$, $Cp_2TiOTiCp^+$, and Cp_2Ti^+. The IR spectrum showed a sharp absorption at 1010 cm^{-1} and a broad band at 1080 cm^{-1} apart from bands assignable to Cp. The ESR spectrum in toluene at room temperature showed a single line at $g = 1.975$.

Reaction of Bis(dicyclopentadienyltitanium) Oxide with Carbon Dioxide. Tetrakis(dicyclopentadienyltitanium) Dicarbonate $[(Cp_2Ti)_4(CO_3)_2]$. Toluene (10 cm^3) was distilled onto $(Cp_2Ti)_2O$ (0.35 g, 0.94

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mmol), giving a dark brown solution. CO_2 (1.04 mmol) was added, the solution becoming green over a period of 0.5 h. It was stirred for a further 15 h, hexane (15 cm^3) added, and the mixture filtered to remove the green precipitate of $[(Cp_2Ti)_4(CO_3)_2]$, which was washed well with hexane, yield 0.28 g (72%). The product had identical physical and chemical properties with the $[(Cp_2Ti)_4(CO_3)_2]$ obtained from the reaction of N_2O with $Cp_2Ti(CO)_2$ (see below) and with that obtained from the reaction between CO_2 and $Cp_2Ti(CO)_2$.[14]

Reaction of Dicyclopentadienyltitanium with Excess Carbon Dioxide. Tetrakis(dicyclopentadienyltitanium) Dicarbonate $[(Cp_2Ti)_4(CO_3)_2]$. A toluene solution of $(Cp_2TiH)_x$ (0.92 g, 5.1 mmol) was stirred at room temperature for 2 h, the evolved H_2 being occasionally pumped away. To the resultant dark green solution of Cp_2Ti was added CO_2 (5.4 mmol). The solution was stirred under CO_2 for 3 days, then the remaining gases were Toeplered, first through the liquid-nitrogen traps (no gas obtained), then through −78 °C traps (CO_2 obtained 1.0 mmol). The green precipitate of $[(Cp_2Ti)_4(CO_3)_2]$ was removed from the solution by filtration, yield 41% based on the equation

$$5Cp_2Ti + 4CO_2 \rightarrow [(Cp_2Ti)_4(CO_3)_2] + Cp_2Ti(CO)_2 \tag{19}$$

The filtrate showed intense absorptions at 1900 and 1975 cm^{-1}, due to $Cp_2Ti(CO)_2$.

Reaction of Dinitrogen Oxide with Dicyclopentadienyltitanium Dicarbonyl. Tetrakis(dicyclopentadienyltitanium) Dicarbonate $[(Cp_2Ti)_4(CO_3)_2]$. In a typical experiment a solution of $Cp_2Ti(CO)_2$ (0.63 g, 2.7 mmol) in toluene (40 cm^3) was heated to 65 °C. Then N_2O (2.0 mmol) was added and the solution stirred for 12 h, after which the solution was purple-blue. The solution was cooled to −78 °C and the gases were Toeplered through liquid N_2 traps (holding back all gases except CO and N_2) into a bulb of known volume. The gases and Toepler pump were isolated from the rest of the line, and the CO and N_2 circulated over a Cu/CuO bed at 300 °C for 3 h. Trapping of the resultant CO_2 in a liquid-nitrogen bath allowed determination of N_2 (0.98 mmol) and by difference the amount of CO (1.45 mmol) produced. These gases were pumped away, and the remaining gases from the reaction (CO_2 and N_2O as shown in separate experiments by IR spectroscopy) Toeplered through −78 °C traps. Circulation of these gases over the Cu/CuO bed converted N_2O to N_2, and hence the amounts of N_2O (1.1 mmol) and CO_2 (in this case <0.15 mmol) were determined. The solvent was removed from the remaining mixture by distillation, and the excess $Cp_2Ti(CO)_2$ (1.70 mmol) sublimed onto a weighed cold finger at 45 °C and 10^{-2} Torr. There was left a pale-green solid, which was redissolved in toluene and filtered, and the filtrate was cooled at −35 °C for 48 h. The green, crystalline precipitate was removed by filtration, yield 0.25 g, 0.3 mmol (60%). Anal. Calcd for $C_{42}H_{40}Ti_4O_6$: C, 60.6; H, 4.8; N, 0; Ti, 23.0. Found: C, 59.3; H, 4.6; N, 0.1; Ti (as TiO_2), 23.7. An average of eight experiments of the type described gave the overall stoichiometry

$$\begin{aligned}1.2(\pm0.4)Cp_2Ti(CO)_2 + 1.2(\pm0.2)N_2O \rightarrow 1.0N_2 + 1.6(\pm0.1)CO +\\ 0.0(\pm0.1)CO_2 + 0.15(\pm0.01)[(Cp_2Ti)_4(CO_3)_2]\end{aligned}$$

Instruments used in this work were a Perkin-Elmer 457 IR spectrophotometer, spectra being measured as Nujol or hexachlorobutadiene mulls or in solution between KBr or CaF_2 plates; a Varian T60 NMR spectrometer; a Hitachi Perkin-Elmer RMU-60 mass spectrometer; and a locally modified version of the Varian E-4 ESR spectrometer. The vacuum line used was a much modified version of that described by Shriver.[35] Microanalyses were by A. Bernhardt, West Germany.

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γ-Radiation–Oxidation of Polycyclic Aromatic Hydrocarbons: Involvement of Singlet Oxygen[1a,b]

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Abstract: Oxidation of organic compounds in the presence of high-energy radiation is generally understood in terms of organic free-radical mechanisms. We investigated the chemistry of certain polycyclic aromatic hydrocarbons in oxygenated solutions submitted to γ-radiation from a cobalt-60 source in an effort to identifity and study other pathways in radiation oxidation. Products obtained could be explained either through singlet oxygen ($^1O_2$) production, through superoxide ($O_2^-\cdot$) production, or through a cation radical mediated reaction with O_2. Quenching experiments clearly established singlet oxygen as the intermediate involved. The oxidation products varied markedly depending on the starting compound. This resulted because the primary endoperoxide adducts were subject to radiation-induced decomposition both by retrograde O_2 expulsion and by breakdown to quinones. It was also found that certain common $^1O_2$ quenchers were ineffective in the radiation environment because of decomposition.

Introduction

Free-radical oxidation mechanisms had been known generally as the classical oxidation route for organic compounds in numerous environments. More recent investigations have brought to light other mechanisms[2] involving "activated forms" of oxygen, including excited-state singlet oxygen ($^1O_2$) and superoxide ($O_2^-\cdot$). The production of these intermediates in a variety of different systems has now been documented; they result,[3,4] for example, from chemical precursors, from photochemical environments, and in biological systems.

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