Reactions of Nitrogen Oxides with Di(cyclopentadienyl)titanium Complexes

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Summary Under various conditions the following reactions between dinitrogen oxide (N_2O) or nitrogen mono-oxide (NO) and di(cyclopentadienyl)titanium (Cp_2Ti) complexes are found: (i) $(Cp_2TiCl)_2 + 2NO \rightarrow (Cp_2TiCl)_2O + N_2O$; (ii) $2Cp_2Ti(CO)_2 + 1NO \rightarrow 3CO +$ Ti-product; (iii) $2Cp_2Ti(CO)_2 + 2NO \rightarrow 2CO + CO_2 + N_2 +$ Ti-product; (iv) $Cp_2Ti(CO)_2 + N_2O \rightarrow N_2 + 2CO + (CpTiO)_x$; (v) $Cp_2Ti(CO)_2 + 2N_2O \rightarrow (CpTiO)_x + CO + CO_2 + 2N_2$; (vi) $CpTi + N_2O \rightarrow (Cp_2Ti)_2O + N_2$.

The reactivity of di(cyclopentadienyl)titanium (Cp_2Ti) complexes towards small molecules such as N_2 and CO is well established.[1,2] However, nothing is known about the behaviour of Cp_2Ti derivatives towards nitrogen oxides such as N_2O or NO. We have begun an investigation of these systems, prompted also by the possibility of concurrent conversion of NO and CO into N_2O and CO_2.

$(Cp_2TiCl)_2$ reacted rapidly and quantitatively with excess of NO in tetrahydrofuran solution at room temperature according to equation (1). When $(Cp_2TiCl)_2$ was in excess

$$(Cp_2TiCl)_2 + 2NO \rightarrow (Cp_2TiCl)_2 + N_2O \qquad (1)$$

small amounts (*ca.* 8%) of N_2 were formed in addition to N_2O. Independent experiments under the same conditions showed that N_2O reacted very slowly with $(Cp_2TiCl)_2$ to form $(Cp_2TiCl)_2O$ and N_2. Reaction (1) proceeded identically in the presence of CO, with no evidence of CO_2 formation.

The reaction between Cp_2Ti and NO in toluene solution proceeded rapidly to form an insoluble polymeric complex of empirical formula Cp_2TiNO.[3] No gaseous products were observed, and the polymeric material $(Cp_2TiNO)_x$ did not react with CO. Cp_2Ti reacts rapidly with CO to form $Cp_2Ti(CO)_2$,[1] and reaction of the latter with NO in toluene solution, with $Cp_2Ti(CO)_2$:NO concentration ratios $> 4:1$, proceeded, in a few hours at 60 °C, according to equation (2).

$$2Cp_2Ti(CO)_2 + 1NO \rightarrow 3CO + \text{Ti-products} \qquad (2)$$

Other than CO no gaseous products were obtained. Two titanium-containing products were obtained: one, an insoluble yellow-brown material, had the properties previously observed for the polymeric material of approximate formula CpTiO obtained when Cp_2Ti solutions are oxidised,[4] and the other was an extremely unstable, tetrahydrofuran-soluble, green complex having a strong i.r. absorption at 2200 cm^{-1}. Because of its instability it has not been possible to characterise this complex fully, but the persistence of the 2200 cm^{-1} absorption even in oxidised or decomposed samples, the presence of up to 4% N in the samples, and the reaction stoicheiometry, indicate the

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presence of a $C\equiv N$– containing unit. In view of the recent finding of the intermediacy of NCO– and CNO– species in the high temperature (500 °C) heterogeneously catalysed oxidation of CO by NO[5] it appears possible that a similar species is formed in the present reaction.

At room temperature, again with a $Cp_2Ti(CO)_2 : NO$ ratio $> 4:1$, the reaction proceeded according to equation (3).

$$2Cp_2Ti(CO)_2 + 2NO \rightarrow 2CO + CO_2 + N_2 + \text{Ti-products} \quad (3)$$

The green material with the strong 2200 cm^{-1} i.r. absorption was again observed as one of the Ti-containing products.

When the $Cp_2Ti(CO)_2 : NO$ ratio was reduced to 2:1 or less, N_2O, as well as N_2, appeared in the gaseous products of the room-temperature reaction. In independent investigations it was found that N_2O reacted with $Cp_2Ti(CO)_2$ in toluene solution at 50 °C, at a rate comparable to that of the reaction of NO with $Cp_2Ti(CO)_2$, according to equation (4).

$$Cp_2Ti(CO)_2 + N_2O \rightarrow N_2 + 2CO + \text{Ti-product} \quad (4)$$

Surprisingly, at lower temperatures we also found CO_2 in the gaseous products. At 5 °C up to 25% of the available CO was converted into CO_2, but at this temperature the reaction required several days. The titanium-containing product of the reactions was the yellow polymer previously described.[4] It contained no nitrogen (by analysis) and showed only i.r. bands assignable to Cp or Ti–O. Because reaction (4) and the reaction producing CO_2 were in competition we are unable to give an equation with certainty, but a reaction such as (5) is implied.

$$Cp_2Ti(CO)_2 + 2N_2O \rightarrow CO + CO_2 + 2N_2 + \text{Ti-product(s)} \quad (5)$$

We also found that at room temperature N_2O acted as a mild oxidizing agent towards Cp_2Ti, rapidly and quantitatively giving the previously unknown Ti^{III} derivative $(Cp_2Ti)_2O$ according to equation (6). The $(Cp_2Ti)_2O$

$$2Cp_2Ti + N_2O \rightarrow (Cp_2Ti)_2O + N_2 \quad (6)$$

complex is orange-brown and was precipitated from toluene by addition of hexane. Interestingly, $(Cp_2Ti)_2O$ undergoes disproportionation in the presence of CO, forming the yellow Ti^{IV} polymer[4] and $Cp_2Ti(CO)_2$, in a manner similar to that proposed for $(Cp_2TiCl)_2$.[6]

Previously reported reactions in which NO and CO were converted into N_2O and CO_2 appear to involve attack of CO on a dinitrosyl complex.[7] For the reaction between $Cp_2Ti(CO)_2$ and NO (which proceeded identically when excess of CO was added with the NO) the following observations indicate that the first step is slow loss of two molecules of CO, presumably with formation of monomeric Cp_2TiNO: (i) the reaction stoicheiometry; (ii) the reaction proceeded more rapidly in the solvent order tetrahydrofuran > toluene > hexane; (iii) at 60 °C or 20 °C with excess of $Cp_2Ti(CO)_2$ both NO and CO were present together over the reaction solution until all the NO was removed by reaction; (iv) i.r. investigation of the reaction between excess of NO and $Cp_2Ti(CO)_2$ in toluene showed that both CO groups were lost essentially simultaneously. Monomeric Cp_2TiNO, which polymerises in the absence of other reaction partners, may then react with excess of $Cp_2Ti(CO)_2$ *via* a binuclear intermediate.

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