Inorganica Chimica Acta, 31 (1978) L443–L444

Catalytic Reduction of Nitric Oxide and Molecular Oxygen by Carbon Monoxide in the Presence of a Platinum(0)–Diphosphine Complex in Solution at Ambient Conditions

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Received September 19, 1978

The recent discovery of a novel Pt(0) dimer, $[Pt_2(\mu\text{-PCP})_3]$, where PCP = $(C_6H_5)_2PCH_2P(C_6H_5)_2$, and its reactions with small molecules (eqn. 1) [1],

$$[Pt_2(\mu\text{-PCP})_3] + nXY \rightarrow [(XY)_nPt_2(\mu\text{-PCP})_3] \quad (1)$$

$$XY = O_2, n = 1; CO, n = 2; NO, n = 3$$

suggested that the complex might catalyze the interactions between these diatomic species. In this note we report some observations, in part preliminary of the title reactions (eqn. 2, 3). Previously, solution catalyzes of these two conversions of environmental

$$2\,NO + CO \xrightarrow[CH_3C_6H_5]{[Pt_2(\mu\text{-PCP})_3]} N_2O + CO_2 \quad (2)$$

$$O_2 + 2CO \xrightarrow[CH_3C_6H_5]{[Pt_2(\mu\text{-PCP})_3]} 2CO_2 \quad (3)$$

importance have been reported only in a few cases: NO + CO by rhodium [2] and iridium [3] complexes and a palladium–copper system [4], and O_2 + CO by $Rh_6(CO)_{16}$ [5, 6]. The catalyses of both of these reactions by the same complex (eqn. 2, 3) appear to be unprecedented.

The experiments were carried out by using 4 X 10^{-3}–2 X 10^{-2} *M* solutions of $[Pt_2(\mu\text{-PCP})_3]$ in toluene ($CH_3C_6H_5$) at 25 °C under a constant total pressure of *ca.* 700 mm. The reactions were followed by gas uptake measurements by standard volumetric techniques (burette-manometer). In order to suppress the pressure of the carbon dioxide produced (eqn. 2, 3) in the closed system, *Ascarite* (NaOH supported on asbestos) was used as an absorbent for CO_2 in a side-arm of the reactor [6]. At the conclusion of the experiments, the gases above the solution were analyzed by gas chromatograph (GC) which indicated the presence of the products as well as the reactants (supplied continuously to the reactor).

All experiments commenced without an induction period. The deep red color of $[Pt_2(\mu\text{-PCP})_3]$ in solution faded when the reactants were mixed, and, in most cases, yellow or light brown precipitates developed within hours, depending on the concentrations of the reactant species[*]. The reactions were followed for periods ranging from 4 to 24 days, and the maximum mole ratios of gas consumed per $[Pt_2(\mu\text{-PCP})_3]$ were (NO + CO):$Pt_2 \approx 80$ and (O_2 + CO):$Pt_2 \approx 40$. The catalytic rates, expressed below in turnover numbers, TN[**], declined steadily with time in all experiments[***].

In the nitric oxide reduction, two different reactant mixtures were used, NO:CO = 1 and NO:CO = 2, but the stoichiometry of the catalysis was the same in both cases (eqn. 2) as shown by GC analysis. However, there were differences in other observations on the two sets of experiments (*cf.* ref. [2]). In the 1:1 case ($p_{NO} = p_{CO}$ = 350 mm), the initial TN was 0.013 min^{-1} [†], and for the 2:1 mixture (p_{NO} = 460, p_{CO} = 230 mm), the corresponding value was 0.007 min^{-1}. Furthermore, the rate of catalysis declined more slowly in experiments with NO:CO = 1 than in those with NO:CO = 2. In the latter case, the reaction stopped after five days, and removal of the gases from the reactor and introduction of a new 2:1 mixture did not revive the catalysis.

All these observations indicate that the reactant nitric oxide is also an inhibitor which converts the catalyst to an inactive species. Stoichiometric reactions of $[Pt_2(\mu\text{-PCP})_3]$ with CO and NO (eqn. 1) agree with this conclusion: while the carbonylation is readily *reversible*, the interaction with NO is *irreversible* under ambient conditions resulting, ultimately, in an apparently different type of Pt–PCP–NO_x complex of unknown nature.

The O_2 + CO reaction (eqn. 3) shows an initial rate of TN = 0.004 min^{-1} and the catalysis essentially

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[*] O_2 and NO adducts of $[Pt_2(\mu\text{-PCP})_3]$ are less soluble than the parent compound.

[**] TN = the number of mol of gas consumed (NO + CO or O_2 + CO) per mole of $[Pt_2(\mu\text{-PCP})_3]$ per minute.

[***] The rate retardation may be attributed to the following factors: (a) under our isobaric conditions the rates, measured by gas uptake, are expected to decrease since the product gas build-up (eqn. 2) lowers the concentrations of the reactants; (b) formation of precipitates which lowers the catalyst concentration; (c) catalyst decomposition, the principal factor (see text).

[†] The IR spectrum (nujol) of a yellow solid isolated after a 10 day catalytic run showed bands at 2122 m and 1330 m, br cm^{-1}, and other absorptions of lower intensity. For comparison, the spectra of the $[Pt_2(\mu\text{-PCP})_3]$ adducts (eqn. 1): CO, 1940 s; NO, 1720 s (initial product) 1350 m and 885 m cm^{-1} (final product) [1].

terminates in 4–5 days[††]. In this case, the inhibitor is obviously molecular oxygen which, separately, reacts irreversibly with $[Pt_2(\mu\text{-PCP})_3]$ (eqn. 1) and produces PCP oxide as a by-product [1]. It appears that the inhibiting roles of NO and O_2 in the respective catalyses might be suppressed by using reactant mixtures in which $[CO] \gg [NO], [O_2]$. This possibility is under investigation, and the work is being extended to test the catalytic activity of other group VIII metal complexes.

The results obtained thus far do not allow a meaningful speculation about the mechanisms of either of the two reactions (eqn. 2, 3). It should be noted however, that the presumed structure of the "initial catalyst", $[Pt_2(\mu\text{-PCP})_3]$, has two terminal vacant metal sites and a potential one for insertion into the Pt–Pt bond [1] which, altoghether, would provide a proximal coordination of the reactants for interaction. Of the two homogeneous catalyses, only the nitric oxide reduction in the presence of a rhodium complex seems to have been studied in a comprehensive detail, and the proposed mechanism involves an intricate series of steps [2b,c].

Acknowledgments

This research was supported by the National Science Foundation (CHE7423405) and the National Institutes of Health (HL-09678).

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[††] The IR spectra of recovered solids exhibited these absorptions in the ν_{CO} region: 2030 m, 1990 s, br, and 1800 s, br cm^{-1}; bands derived from PCP oxide and other (unidentified) lower frequency absorptions were also evident; the ν_{O_2} of $[(O_2)Pt(\mu\text{-PCP})_3]$ at 827 cm^{-1} [1] was absent.