

Preliminary communication

EVIDENCE FOR CATALYTIC ACTIVITY BY LOWER NUCLEARITY RHODIUM CARBONYLS IN THE $\text{Rh}_6(\text{CO})_{16}$ CATALYZED OXIDATION OF CYCLOHEXANONE WITH MOLECULAR OXYGEN

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Summary

The yield of carboxylic acid in the $\text{Rh}_6(\text{CO})_{16}$ catalyzed oxidation of cyclohexanone with molecular oxygen is higher with increasing CO pressure. The data are interpreted as providing support for a lower nuclearity rhodium carbonyl complex being involved as the reactive intermediate in the catalytic cycle.

Recently we reported that $\text{Rh}_6(\text{CO})_{16}$ is an effective homogeneous catalyst for the oxidation of CO to CO_2 and of ketones to carboxylic acids with molecular oxygen [1]. The cluster compound was designated a catalyst because it was recovered from the reaction, but no inference was made that the hexarhodium cluster remained intact during the catalytic cycle. In view of the thriving interest in the use of transition metal cluster compounds as homogeneous catalysts [2], it is obviously of importance to try and probe the mechanistic function of $\text{Rh}_6(\text{CO})_{16}$ in these reactions. If particular carbonylrhodium(0) compounds are especially active catalytically, we expect that the product yield will be influenced by changes in carbon monoxide pressure.

In Table 1 are shown our preliminary data on the conversion of cyclohexanone into carboxylic acid. These data* have been obtained at $85 \pm 1^\circ\text{C}$ and under isobaric conditions of $650 \pm 20 \text{ lb. in}^{-2}$. This condition is created by changing the partial pressure ratio of CO in a mixture of CO and O_2 between 0.42 and 0.89. The data in Table 1 are arranged to show the effect on acid yield of changing the CO and O_2 pressure in a solution containing $\text{Rh}_6(\text{CO})_{16}$ cyclohexanone**. Data for both 10 and 12 h reaction times are given, and in Fig. 1 we plot the 12 h data for acid yield (mmol) against both oxygen pressure and

*The reaction mixture is placed in a glass vial in a Parr Model 4702 high pressure reaction vessel fitted with a 45 ml cup and a 5000 psig gauge. The mixture is stirred magnetically. The total acid content is determined by titration.

**Previously we have shown that the acid product from this oxidation is adipic acid [1].

TABLE 1

ACID PRODUCED USING $\text{Rh}_6(\text{CO})_{16}$ WITH CHANGING PRESSURES OF CO AND O_2 ,
TEMPERATURE 85°C , CYCLOHEXANONE (10 ml)

$p(\text{CO})$ (lb. in $^{-2}$)	$p(\text{O}_2)$ (lb. in $^{-2}$)	$p(\text{CO})$ $p(\text{total})$	Acid (mmol)	Time (h)
340	330	0.51	1.10	10
440	220	0.67	1.37	10
520	140	0.79	1.71	10
540	100	0.84	1.94	10
555	70	0.89	2.04	10
280	380	0.42	1.76	12
500	160	0.76	2.65	12
520	110	0.83	2.84	12
550	80	0.87	2.96	12

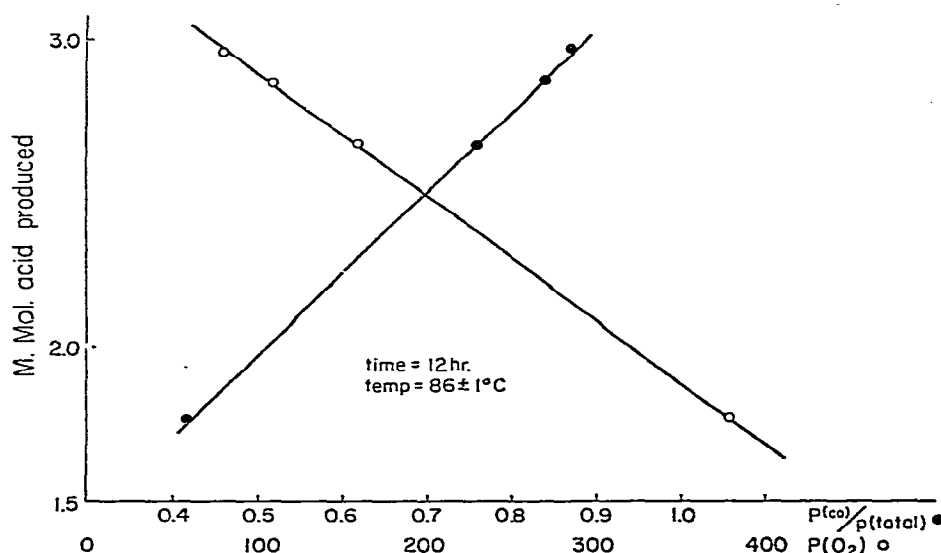


Fig. 1. Plot of data in Table 1 for acid yield (mmol) against both oxygen pressure and the carbon monoxide fractional pressure.

the CO pressure. These data show that as the oxygen pressure decreases, or concurrently as the CO pressure increases, under isobaric conditions, there is an increase in the quantity of carboxylic acid formed. This result is unexpected since lowering the partial pressure of oxygen creates a situation where its concentration becomes increasingly deficit for its function as a reactant for the conversion of both CO to CO_2 and cyclohexanone to adipic acid. It is apparent, therefore, that there is an increase in catalytic activity as the pressure of CO is raised. In magnitude, the yield of carboxylic acid increases from 1.76 mmol to 2.96 mmol* on lowering the oxygen pressure from 380 to 80 lb. in $^{-2}$. In Table 2

*Under identical experimental conditions in the absence of $\text{Rh}_6(\text{CO})_{16}$, the yield of carboxylic acid is 0.75 (± 0.25) mmol.

TABLE 2

ACID PRODUCED USING $\text{Re}_2(\text{CO})_{10}$ (50 mg) WITH CHANGING PRESSURES OF O_2 ,
TEMPERATURE 115°C , CYCLOHEXANONE (5 ml) AND ACETONE (10 ml)

$p(\text{O}_2)$ (lb. in $^{-2}$)	Acid (mmol)	Time (h)
300	10.7	20
400	15.4	18
500	20.8	15.5

we show the data obtained for $\text{Re}_2(\text{CO})_{10}$. In this case there is an expected increase in acid yield as the pressure of oxygen* in the reaction is changed from 300 to 500 lb. in $^{-2}$.

The most reasonable explanation for these data is that under the increasing CO pressure there is a corresponding increase in the concentration of a lower nuclearity rhodium carbonyl compound which is the catalytically active species in the reaction mixture**. This concept is in agreement with previous ideas that smaller aggregate carbonyl clusters are formed under high CO pressure [3]. In particular for rhodium(0), Whyman has shown that under an extremely high pressure of CO there is a conversion to the dimeric compound $\text{Rh}_2(\text{CO})_8$ [4]. Under our experimental conditions it is not possible to directly observe such intermediates and no attempt has yet been made to do so. We have, however, previously used the lower cluster compound $\text{Rh}_4(\text{CO})_{12}$ as a catalyst for the oxidation of cyclohexanone. The results show that the compound is effective as a catalyst, but is converted to $\text{Rh}_6(\text{CO})_{16}$ and is not recoverable as $\text{Rh}_4(\text{CO})_{12}$ [1].

The chemistry and function of $\text{Rh}_6(\text{CO})_{16}$ as a labile multisubstrate oxidation catalyst for carbon monoxide, triphenylphosphine and organic compounds is under continuing investigation, and details will be published later.

Acknowledgments

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*In this case there is no CO pressure. The complex $\text{Re}_2(\text{CO})_{10}$ is recovered unchanged.

**Attempts to verify this by kinetic measurements have not proven possible because of sampling problems during the reaction sequence. The reaction is an autoxidation under high pressure and sample removal cannot be done under our experimental conditions without perturbing the reaction progress.

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