mum E_S value obtained in our analysis could actually be lower by several kcal mol^{-1}.

(22) From ref 16, $E(C_{co}-C_d) = (E(C_{co}-C) + E(C_d-C))/2 = (-9.23 - 4.62)/2 = -6.93$; $E(C_d-C_b) = (E(C_d-C) + E(C_b-C))/2 = (-4.62 - 3.46)/2 = -4.04$.

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Transfer Hydrogenation in the Presence of a Homogeneous Rhodium Catalyst

C. Masters,* A. A. Kiffen, and J. P. Visser

Contribution from Shell Research B.V., Koninklijke/Shell-Laboratorium, Amsterdam, The Netherlands. *Received January 27, 1975*

Abstract: Complexes formed by addition of a tertiary phosphine to a solution of tetra(cyclooctene)di-μ-chloro-dirhodium(I) in 1,4-dioxane function as active catalysts for the transfer of hydrogen from the dioxane to a suitable olefin. The catalytic activity is dependent upon the nature of the tertiary phosphine ligand, with trialkylphosphines giving rise to the most active catalysts. The preferred tertiary phosphine to rhodium ratio is 2 and any deviation from this ratio results, except with triphenylphosphine, in a marked decrease in catalytic activity. A range of olefins is shown to be effective as hydrogen acceptors. Of the aliphatic olefins tested cyclopentene was the most effective and of the aromatic olefins, styrene. Several substrates other than 1,4-dioxane were tested as hydrogen donors, but none of them was capable of matching the activity of this compound. Transfer of hydrogen between the organic groups of the tertiary phosphine ligands and the cyclopentene is shown to occur during the transfer-hydrogenation reaction although this appears to be incidental to the main reactions. The kinetics of the hydrogen-transfer reaction between 1,4-dioxane and cyclopentene catalyzed by either the $RhCl(PPh_3)_3$ or Rh_2Cl_2(cyclooctene)$_4$-$4PEt_3$ system are reported. Although the reaction is at first sight first order in cyclopentene, the observed first-order rate constant is not independent of the initial cyclopentene concentration, $[C]_0$, but decreases as $[C]_0$ increases. It is proposed that the apparent first-order dependence on cyclopentene is due to a competitive inhibition step involving reversible complex formation between either 1,4-dioxene (product) or cyclopentene and the catalyst. It is suggested that the nonintegral order in catalyst, 0.73 ± 0.04 for Rh_2Cl_2(cyclooctene)$_4$-$4PEt_3$ and 0.85 ± 0.04 for $RhCl(PPh_3)_3$, is due to the rhodium complex being present, to a small extent, as a dimeric species. With $RhCl(PPh_3)_3$ as catalyst, dioxane-solvated chloro-bridged dimeric rhodium complexes of the type $Rh_2Cl_2(PPh_3)_4 \cdot x$(dioxane), where $x = 1-2$, were isolated from the reaction mixture.

Interactions between a carbon–hydrogen bond and a metal center in both heterogeneous[1] and homogeneous[2] systems are currently the subject of much study. The finding that $RhCl(PPh_3)_3$ catalyzes the transfer of hydrogen from the saturated ether 1,4-dioxane to cyclopentene[3] prompted us, in view of our interest in reactions occurring at a saturated C–H bond,[4,5] to investigate this reaction in some detail.

Some months after we had completed our study Nishiguchi and Fukuzumi reported[6] in detail on the $RhCl(PPh_3)_3$-catalyzed transfer-hydrogenation reaction. Our results differ considerably from theirs and, we believe, shed more light on this interesting, and potentially important reaction.

Results

(a) Catalyst Modifications. In studying (i) the importance of the tertiary phosphine to rhodium ratio, and (ii) the effect of the nature of the tertiary phosphine ligand on the catalytic activity, we have made use of the fact that in the tetra(cyclooctene)di-μ-chloro-dirhodium(I)–tertiary phosphine system[7,8] the cyclooctene ligands are easily replaced, and the chloro bridge is readily split, by tertiary phosphines.

(i) **Variation of the Tertiary Phosphine to Rhodium Ratio.** Under standard conditions (see Experimental Section) we varied the tertiary phosphine:rhodium ratio. It can be seen from the results given in Table I that when L = PPh_3 the catalytic activity increases with the L:Rh ratio, reaching a maximum at ca. 3. In agreement with the result reported by Nishiguchi et al.,[6] we find that adding more triphenylphosphine has no measurable effect on the performance of the catalyst. However, with the other tertiary phosphines tested a maximum catalytic activity is observed with a L:Rh ratio of 2:1 and addition of more tertiary phosphine results in a decrease in activity. At Rh:L ratios below 1:2 the solution did not, under the reaction conditions, remain homogeneous but deposited rhodium metal.

The decrease in activity in the presence of excess tertiary phosphine indicates that, with the exception of triphenylphosphine,[6] the tertiary phosphines can effectively compete with solvent dioxane for vacant coordination sites on the rhodium. The observation that the decrease is more marked for the dialkylphenylphosphines than for the diphenylalkylphosphine ligands may reflect the stronger bonding properties of the former.

(ii) **Variation of the Tertiary Phosphine Ligand.** The data we obtained using a wide range of tertiary phosphine ligands, in an attempt to understand some of the factors influencing the catalytic activity, are summarized in Table II.

The first five results in this table show that, whereas electron-withdrawing substituents (i.e., F) in the aromatic ring of the triarylphosphine ligand cause a marked decrease in activity, electron-donating substituents (i.e., CH_3) cause a slight increase. With this in mind we investigated catalyst systems involving more basic, electron-releasing, tertiary phosphine ligands.

The remaining data in Table II show that for the mixed arylalkylphosphines replacement of phenyl by either ethyl or propyl leads to an increase in activity. Similarly triethyl-,

Table I. Effect of Tertiary Phosphine (L) to Rhodium Ratio on the Catalytic Transfer of Hydrogen from 1,4-Dioxane to Cyclopentene[a]

L	% conversion (±3%) of cyclopentene to cyclopentane at the Rh:L ratios indicated				
	1:1[c]	1:2	1:3	1:4	1:5
PPh_3	<1	42	54	56	52
PPh_2Me	<1	20	10		
PPh_2Et	4	50	45		
PPh_2Pr	<1	49	41		
$PPhMe_2$	<1	17	1		
$PPhEt_2$	4	45	24		
PEt_3[b]	13	66	40	17	9

[a] Catalyst (0.02 M) in 1,4-dioxane containing cyclopentene (0.5 M) (reaction temp, 180 °C; reaction time 30 min). Catalyst prepared in situ by adding the tertiary phosphine to bis(cyclooctene)chlororhodium(I) dimer in 1,4-dioxane under argon (0.02 M with respect to Rh). [b] Reaction time 15 min. [c] Solution failed to remain homogeneous throughout the reaction; some metal deposited.

Table II. Effect of Tertiary Phosphine Ligands on the Rhodium-Catalyzed Transfer of Hydrogen from 1,4-Dioxane to Cyclopentene[a]

L	% conversion (±3%) of cyclopentene to cyclopentane after 30 min	after 15 min
PPh_3	41	
$P(o\text{-}CH_3C_6H_4)_3$	46	
$P(p\text{-}CH_3C_6H_4)_3$	43	
$P(p\text{-}FC_6H_4)_3$	11	
$P(m\text{-}FC_6H_4)_3$	20	
PPh_2Me	19	
$PPhMe_2$	13	
PPh_2Et	50	
$PPhEt_2$	45	
PPh_2Pr	49	
PMe_3	31	16
PEt_3	91	62
PPr_3	93	69
PBu_3	83	47

[a] Catalyst (0.02 M) in 1,4-dioxane containing cyclopentene (0.5 M); reaction temp 180 °C. Catalyst prepared in situ by adding the tertiary phosphine (2 molar equiv *per* rhodium) to bis(cyclooctene)chlororhodium(I) dimer in 1,4-dioxane under argon (0.02 M with respect to Rh).

tripropyl-, and tributylphosphine give rise to extremely active catalysts. The picture is, however, confused by the results obtained with the methyl-substituted tertiary phosphine ligands. Contrary to what might be expected on the basis of their electron-donating properties, trimethyl-, dimethylphenyl-, and methyldiphenylphosphine all give rise to catalysts of low activity. We are unable, at the present time, to explain this observation. We originally considered that internal metalation of the alkyl group(s) of the tertiary phosphine ligand, similar to that previously found[5] in tertiary phosphine complexes of platinum(II), played an essential role in the reaction. The low activity observed with the methyl-substituted tertiary phosphines could then be attributed to the methyl group having to form a highly strained three-membered ring system in the internally metalated intermediate. We have shown that this is not the case by using four deuterated tertiary phosphine ligands, viz., $P(C_6D_5)_3$, $P(C_6H_5)_2CD_3$, $P(C_6H_5)_2C_2D_5$, and $P(C_2D_5)_3$, and analyzing the cyclopentene-cyclopentane recovered after reaction for deuterium. The results, given in Table III, show that although internal metalation of the tertiary phosphine occurs during the transfer-hydrogenation reaction, it is not an essential constituent of this reaction. For instance, although diphenylethylphosphine forms a much more active catalyst than diphenylmethylphosphine after approximately the same percent conversion of cyclopentene to cyclopentane (results 4 and 5), the deuterium transfer from the two tertiary phosphines is approximately the same. If internal metalation were playing an important role one would expect more deuterium transfer from the diphenylethylphosphine than from the diphenylmethylphosphine. Similar reasoning may be applied to results 1 and 7 for the triphenyl- and triethylphosphines, respectively. We further found that the use of deuterated tertiary phosphine ligands had no effect on the rate of the reaction, i.e., resulted in no appreciable isotope effect.

Of the other ligands tested, viz., NPh_3, $AsPh_3$, $SbPh_3$, $BiPh_3$, $P(OEt)_3$, $P(OPh)_3$, and $Ph_2PCH_2CH_2PPH_2$, none gave rise to active catalysts when added to tetra(cyclooctene)di-μ-chloro-dirhodium(I).

(iii) **Catalysts of Type $RhX(PPh_3)_3$, Where X = Cl, Br, or I.** We tested three complexes of type $RhX(PPh_3)_3$[9], viz., with X = Cl, Br, and I, as transfer-hydrogenation catalysts. The order of activity is Br > Cl > I. The position of the iodide complex is, however, of limited significance since, under the reaction conditions, it decomposes to a considerable extent.

(iv) **Other Catalyst Systems.** We tested a number of other systems as transfer-hydrogenation catalysts. As can be seen from the results in Table IV none of the complexes tested approached the catalytic activity of the Rh_2Cl_2(cyclooctene)$_4$–4PEt_3 system.

(b) **Changes in Hydrogen Acceptor.** Using dioxane as the hydrogen donor we tested a range of olefins as hydrogen acceptors. The results are given in Table V (the data for cyclopentene are quoted at two temperatures, viz., 180 and 160 °C, to allow a comparison to be made between the two sets of data in Table V). With the cycloolefins the ability to act as a hydrogen acceptor decreased above C-8 and with the linear olefins a similar decrease was observed above C-6. As to the lower olefins, butene-1 and propene-1 showed about the same activity as cyclopentene, but ethene proved to be a poor acceptor, having no more than about one-fifth the activity of cyclopentene.

Table III. Transfer of Deuterium between the Tertiary Phosphines of the Rhodium Catalyst[a] and Cyclopentene–Cyclopentane during the Catalytic Transfer of Hydrogen from 1,4-Dioxane to Cyclopentene at 180 °C

Result no.	1	2	3	4	5	6	7	8
Tertiary phosphine	$P(C_6D_5)_3$	$P(C_6D_5)_3$	PPh_2CD_3	PPh_2CD_3	$PPh_2C_2D_5$	$PPh_2C_2D_5$	$P(C_2D_5)_3$	$P(C_2D_5)_3$
Reaction time, h	1.25	2	5	8	1	3	0.2	0.5
% conversion of cyclopentene to cyclopentane	58	66	29	43	55	95	59	94
Deuteration, %[b]								
Cyclopentene d_0	90	85	97	97	98	93	99	92
d_1	9	12	2	2	1	5	1	8
d_2	0.5	1	1	0.5	0	1	0	0
Cyclopentane d_0	*c*	95	100	*c*	100	*c*	*c*	*c*
d_1	*c*	5	<0.5	*c*	<0.5	*c*	*c*	*c*
d_2	*c*	0.5	<0.5	*c*	<0.5	*c*	*c*	*c*

[a] Catalyst prepared in situ by adding the tertiary phosphine (2 molar equiv per rhodium) to bis(cyclooctene)chlororhodium(I) dimer in 1,4-dioxane under argon (0.02 M with respect to Rh). [b] ±0.5%. [c] Not measured.

Table IV. Other Complexes as Catalysts for the Transfer of Hydrogen from 1,4-Dioxane to Cyclopentene[i]

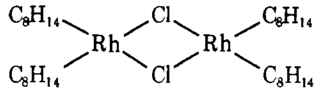
Complex or catalyst system	Reaction time, h	% conversion (±3%) of cyclopentene to cyclopentane
$[Rh(CO)_2Cl]_2$[a][10]	1	<1
$[RhCl(CO)(P\text{-}t\text{-}Bu_3)]_2$[a][11]	1	<1
$RhClH_2(P\text{-}t\text{-}Bu_3)_2$[a,b][12]	2	<1
$Rh(OAc)(PPh_3)_3$[13]	1/2	6
$IrH_5(PPhEt_2)_2$[b][14]	1/2	6[c]
$IrH_5(PPr_3)_2$[b][14]	1/2	5[c]
$IrH_5(PPr_3)_2$	1/2	16[d]
$[IrCl(C_8H_{14})_2]_2$[e][15] + $2PPh_3$	1/2	6
$[IrCl(C_8H_{14})_2]_2$[e] + $2PEt_3$	1/2	2
$RuCl_2(PPh_3)_3$[16]	1/2	<1
$(\pi\text{-}C_5H_5)_2TaH_3$[17]	1/2	4[c]
$(\pi\text{-}C_5H_5)_2TaH_3 + PEt_3$	66	5[c]
$(\pi\text{-}C_5H_5)_2TaH_3 + 2PEt_3$	1/2	2[c]
$CoCl_2 + 2PPh_3$[f]	1/2	<1
$RhCl_3 \cdot 3H_2O + 2PPh_3$[f]	1/2	5
$IrCl_3 + 2PPh_3$[f]	1/2	<1
$NiCl_2 + 2PPh_3$[f]	1/2	<1
$PdCl_2 + 2PPh_3$[f]	1/2	<1
$PtCl_2 + 2PPh_3$[f]	1/2	<1
$FeCl_24H_2O + 2PPh_3$[f]	1/2	<1
$RuCl_33H_2O + 2PPh_3$[f]	1/2	<1
$CuCl(PPh_3)_3$[g][18]	1/2	<1
$FeCl_2(PPh_3)_2$[19]	1/2	<1
$CoCl(PPh_3)_3$[20]	1/2	<1
$CoCl_2(PPh_3)_2$[21]	1/2	<1
$CoH_3(PPh_3)_2$[a][22]	1/2	7[a]
$CoH_3(PPh_3)_2$[h]	64	8[c]

[a] Decomposed in the course of the reaction. [b] Reaction temp 100 °C. [c] Hydrogenation resulting from hydride ligands on the complex; no dehydrogenation of dioxane. [d] Only 8% dioxane formed. [e] C_8H_{14} is cyclooctene. [f] Reaction mixture nonhomogeneous. [g] Reaction temp 160 °C. [h] Reaction temp 70 °C. [i] Complex, or catalyst system (0.02 M), in dioxane containing cyclopentene (0.5 M); reaction temp. 180 °C.

Table V also contains the results obtained using various substituted styrenes as hydrogen acceptors. As can be seen from the data styrene proved to be slightly superior to cyclopentene as a hydrogen acceptor; however, ring substitutions designed to alter the electronic characteristics of the styrene double bond had no drastic effect on the reaction.

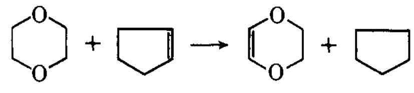
(c) Changes in Hydrogen Donor. We tested a number of nonalcoholic substrates other than dioxane as hydrogen donors. The results, given in Table VI, show that all the compounds tested were far inferior to dioxane in their ability to act as hydrogen donors.

(d) Kinetic Results. As reported in section (a), the complex formed from bis(cyclooctene)chlororhodium(I) dimer (I) and 4 molar equiv of triethylphosphine is our most active catalyst for the transfer of hydrogen from dioxane to cyclopentene. We therefore decided to confine our kinetic study to this system. A few months after completion of our work, Nishiguchi and Fukuzumi reported kinetic data for this reaction using chlorotris(triphenylphosphine)rhodium(I) as catalyst.[6] Since their results differed considerably from those obtained by us with $[Rh_2Cl_2(cyclooctene)_4]$-$4PEt_3$, we repeated our measurements using $RhCl(PPh_3)_3$.



We here report and compare the two sets of data and endeavor to clarify the differences, both in results and in interpretation, between our observations and those of Nishiguchi et al.

Reaction 1 was studied over the temperature range of


(1)

140–180 °C with either $[Rh_2Cl_2(cyclooctene)_4]$-$4PEt_3$ or $RhCl(PPh_3)_3$ as the catalyst (see Experimental Section). The rate data were obtained by measuring the percentage conversion of cyclopentene to cyclopentane (x) using GLC. Determination (NMR) of the dioxene formed during the reaction showed that, within experimental error, dioxene

Table V. Effect of Hydrogen Acceptor on the Catalytic Transfer Hydrogenation Involving 1,4-Dioxane as Hydrogen Donor[c]

Hydrogen acceptor	Reaction temp., °C	% conversion (±5%), i.e., hydrogenation of hydrogen acceptor
	Catalyst A	
Cyclopentene	180	86
Pentene-1	180	72
Pentene-2[a]	180	73
Hexene-1	180	66
Hexene-3	180	63[b]
Heptene-1	180	50[b]
Cyclopentene	160	51
Cyclohexene	160	52
Cycloheptene	160	56
Cyclooctene	160	30
Cyclodecene	160	22
Cyclododecene	160	5
	Catalyst B	
Cyclopentene	180	42
Styrene	180	58
p-F-styrene	180	56
p-Cl-styrene	180	45
p-Me-styrene	180	50
m-Me-styrene	180	55
p-MeO-styrene	180	48
α-Me-styrene	180	44
cis-Stilbene	180	47

[a] Mixture of cis and trans. [b] Some isomerization of the olefin occurred during the reaction. [c] Catalyst (0.02 M) in dioxane containing the hydrogen acceptor (0.5 M); reaction time 30 min. Catalyst A; prepared in situ by adding triethylphosphine (2 molar equivalents *per* rhodium) to bis(cyclooctene)chlororhodium(I) dimer in dioxane under argon (0.02 M with respect to Rh). Catalyst B: $RhCl(PPh_3)_3$.

Table VI. Effect of Hydrogen Donor on the Catalytic Transfer Hydrogenation Involving Cyclopentene as Hydrogen Acceptor[a]

Hydrogen donor	Catalyst system[a]	% conversion (±3%) of cyclopentene to cyclopentane
Dioxane	A	53
Oxane	A	<2
1,4-Dimethylpiperazine	A	16
4-Methylmorpholine	A	4
Diglyme	A[b]	14
Dioxane	B	91
1,2-Dimethoxyethane	B	9
1,2-Diethoxyethane	B	7
1,2-Diacetatoethane	B	3
2,2-Diacetatoethane	B	6
1,2-Dimethoxycyclohexane[c]	B	<2

[a] Catalyst (0.02 M) in hydrogen-donor containing cyclopentene (0.5 M); reaction temp. 180 °C, reaction time 30 min. Catalyst system A = $RhCl(PPh_3)_3$; 0.02 M with respect to Rh. Catalyst system B prepared in situ by adding triethylphosphine (2 molar equiv *per* rhodium) to bis(cyclooctene)chlororhodium(I) dimer in hydrogen donor under argon (0.02 M with respect to Rh). [b] Reaction time 63 h. [c] 40% cis and 60% trans mixture.

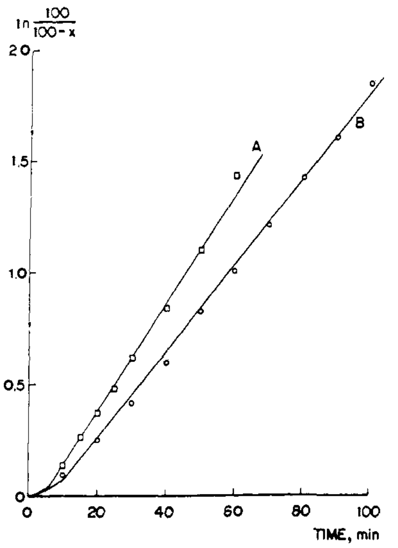


Figure 1. Plot of ln (100/(100 − x)), where x = percentage conversion of cyclopentene to cyclopentane vs. time for the rhodium-catalyzed hydrogen transfer between dioxane and cyclopentene: catalyst A, $Rh_2Cl_2(cyclooctene)_4$-4PEt_3, (0.02 M with respect to Rh, see Experimental Section) in dioxane containing cyclopentene (0.48 M), reaction temperature 160 °C; catalyst B, $RhCl(PPh_3)_3$ (0.02 M) in dioxane containing cyclopentane (0.5 M), reaction temperature 170 °C.

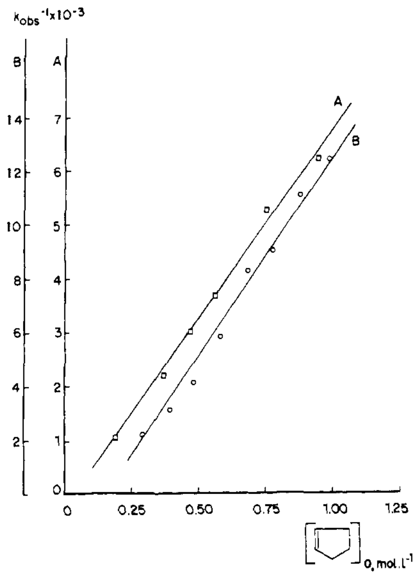


Figure 2. Plot of the inverse of the observed pseudo-first-order rate constant vs. the initial cyclopentene concentration for the rhodium-catalyzed hydrogen transfer between dioxane and cyclopentene: catalyst A, $Rh_2Cl_2(cyclooctene)_4$-4PEt_3, (0.02 M with respect to Rh, see Experimental Section) in dioxane containing cyclopentene, reaction temperature 160 °C; catalyst B, $RhCl(PPh_3)_3$ (0.02 M) in dioxane containing cyclopentene, reaction temperature 170 °C.

Table VII. Dependence of the Pseudo-First-Order Rate Constants, k_{obsd} on the Initial Cyclopentene Concentration $[C_5H_8]_0$, in the Rhodium-Catalyzed Hydrogen Transfer between 1,4-Dioxane and Cyclopentene

$[C_5H_8]_0$,[a] mol L.$^{-1}$	10^4k_{obsd},[b] s^{-1} Catalyst A	10^4k_{obsd},[b] s^{-1} Catalyst B
0.19	9.5	
0.29		4.4
0.37	4.5	
0.39		3.2
0.47	3.3	
0.48		2.4
0.56	2.7	
0.58		1.7
0.68		1.2
0.75	1.9	
0.77		1.1
0.87		0.9
0.94	1.6	
0.97		0.8

[a] Corrected for the cyclopentene present in the gas phase at the reaction temperature (ca. 3.0%). [b] Catalyst (A) $Rh_2Cl_2(cyclooctene)_4$–4PEt_3, (0.02 M with respect to Rh, see Experimental Section) in dioxane containing cyclopentene, reaction temperature 160 °C; (B) $RhCl(PPh_3)_3$, (0.02 M) in dioxane containing cyclopentene, reaction temperature 170 °C. Estimated error not greater than 10% (see text).

Table VIII. Effect of Added Dioxene on the Pseudo-First-Order Rate Constant, k_{obsd}, in the Rhodium-Catalyzed Hydrogen Transfer between 1,4-Dioxane and Cyclopentene

[Dioxene]$_0$, mol L^{-1}	10^4k_{obsd},[a] s^{-1} Catalyst A	10^4k_{obsd},[a] s^{-1} Catalyst B
0	3.1	2.7
0.1	2.7	2.3
0.2	2.3	2.2
0.3	2.0	1.8
0.4	1.8	1.6
0.5	1.7	1.4

[a] Catalyst (A) $Rh_2Cl_2(cyclooctene)_4$–4PEt_3, (0.02 M with respect to Rh, see Experimental Section) in dioxane containing cyclopentene (0.48 M) and dioxene, reaction temperature 160 °C; (B) $RhCl(PPh_3)_3$ (0.02 M) in dioxane containing cyclopentene (0.5 M) and dioxene, reaction temperature 170 °C. Estimated error not greater than 10% (see text).

and cyclopentane were formed in equal amounts, thus establishing the 1:1 stoichiometry of the transfer-hydrogenation reaction.

For both catalyst systems a plot of ln (100/(100 − x)) vs. time[23] is linear up to ca. 80% conversion of cyclopentene to cyclopentane (see Figure 1), indicating that the reaction is first order in cyclopentene. However, as can be seen from the data in Table VII, the observed first-order rate constant, k_{obsd}, is *not* independent of the initial cyclopentene concentration,[24] $[C]_0$, but decreases as $[C]_0$ is increased such that a plot of k^{-1}_{obsd} vs. $[C]_0$ is linear (see Figure 2). Similarly, as can be seen from the data presented in Table VIII, addition of one of the reaction products, dioxene, to the reaction mixture causes a decrease in k_{obsd} such that a plot of k^{-1}_{obsd} vs. $[P]_0$, where $[P]_0$ represents the initial dioxene concentration, is linear (see Figure 3).

We have measured the apparent first-order rate constants as a function of initial rhodium complex concentrations. A least-squares analysis of the data shown in Figure 4 indicates that the reaction orders are 0.85 ± 0.04[25] and 0.73 ± 0.04 in $RhCl(PPh_3)_3$ and $Rh_2Cl_2(cyclooctene)_4$-4PEt_3, respectively.

In agreement with the observations of Nishiguchi et al.,[6] we find that, with toluene[26] as a cosolvent, a plot of k_{obsd} vs. dioxane concentration is linear (see Figure 5), indicating that the transfer-hydrogenation reaction is first order in dioxane.

Temperature studies over the range of 140–180 °C (see Table IX) give values of 25 ± 2 and 30 ± 2[27] kcal mol^{-1} for the overall energies of activation for the reactions catalyzed by $Rh_2Cl_2(C_8H_{14})_4$-4PEt_3 and $RhCl(PPh_3)_3$, respectively.

Using octadeuteriodioxane, in place of dioxane, with $Rh_2Cl_2(C_8H_{14})_4$-4PEt_3 as the catalyst resulted, at 180 °C, in a 69% decrease in observed rate constant, which corresponds to a kinetic isotope effect $k_{obsd}(H)/k_{obsd}(D)$ of 3.2 ± 0.5.[28]

(e) Complex Isolated after the Reaction. Nishiguchi and Fukuzumi found[6] that, after the reactions in dioxane, with

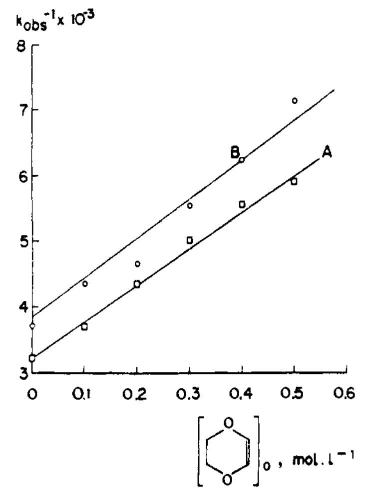


Figure 3. Plot of the inverse of the observed pseudo-first-order rate constant vs. the initial dioxene concentration for the rhodium-catalyzed hydrogen transfer between dioxane and cyclopentene: catalyst A, $Rh_2Cl_2(cyclooctene)_4$-4PEt_3 (0.02 M with respect to Rh, see Experimental Section) in dioxane containing cyclopentene (0.48 M), reaction temperature 160 °C; catalyst B, $RhCl(PPh_3)_3$ (0.02 M) in dioxane containing cyclopentene (0.5 M), reaction temperature: 170 °C.

Table IX. Observed Pseudo-First-Order Rate Constant (k_{obsd}) for the Rhodium-Catalyzed Hydrogen Transfer between 1,4-Dioxane and Cyclopentene as a Function of Reaction Temperature

Temp, ±1 K	$10^4 k_{obsd}$,[a] s^{-1} Catalyst A	k_{obsd},[a] s^{-1} Catalyst B
413	0.16	0.8
423	0.42	1.6
433	1.1	3.1
443	2.3	10.6
453	4.2	—

[a] Catalyst (A) $Rh_2Cl_2(cyclooctene)_4$-4PEt_3 (0.02 M with respect to Rh, see Experimental Section) in dioxane containing cyclopentene (0.48 M); (B) $RhCl(PPh_3)_3$ (0.02 M) in dioxane containing cyclopentene (0.5 M). Estimated error not greater than 10% (see text).

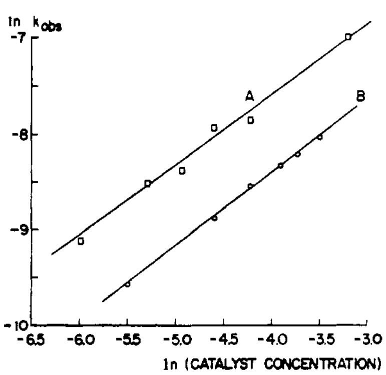


Figure 4. Plot of ln (catalyst concentration) vs. ln (k_{obsd}) for the rhodium-catalyzed hydrogen transfer between dioxane and cyclopentene: catalyst A, $Rh_2Cl_2(cyclooctene)_4$-4PEt_3 (see Experimental Section) in dioxane containing cyclopentene (0.48 M), reaction temperature 160 °C; catalyst B, $RhCl(PPh_3)_3$ in dioxane containing cyclopentene (0.5 M), reaction temperature 170 °C.

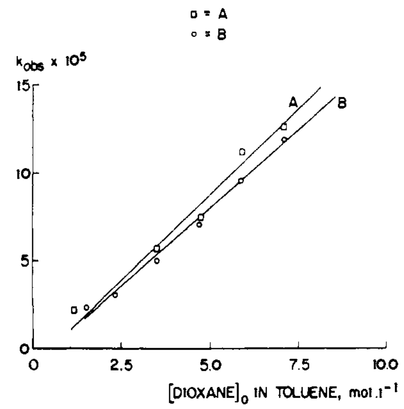


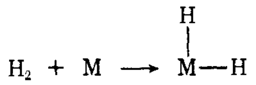
Figure 5. Plot of the observed pseudo-first-order rate constant, k_{obsd}. vs. the concentration of dioxane in toluene for the rhodium-catalyzed hydrogen transfer between dioxane and cyclopentene: catalyst A, $Rh_2Cl_2(cyclooctene)_4$-PEt_3 (0.02 M with respect to Rh, see Experimental Section) in toluene containing dioxane and cyclopentene (0.5 M), reaction temperature 160 °C; catalyst B, $RhCl(PPh_3)_3$ (0.02 M) in toluene containing dioxane and cyclopentene (0.5 M), reaction temperature 170 °C.

$RhCl(PPh_3)_3$ as the catalyst, orange-red needles (A) were isolated when the reaction mixtures were left at room temperature. On the basis of elemental analysis, infrared, and ^1H NMR they suggested that A is $RhCl(PPh_3)_2(C_4H_8O_2)$, formed by replacing a triphenylphosphine of $RhCl(PPh_3)_3$ by a dioxane molecule. They further observed that on warming in dioxane $RhCl(PPh_3)_3$ gave $RhCl(PPh_3)_2(C_4H_8O_2)$, i.e., A, rather than, as reported by Wilkinson et al.,[29] the chloro-bridged dimer $[RhCl(PPh_3)_2]_2$.

We have been unable to isolate complex A from either the transfer-hydrogenation reaction mixture or a refluxed solution of $RhCl(PPh_3)_3$ in dioxane. In both cases we obtained the chloro-bridged dimer containing dioxane occluded in the crystal structure. As previously stated,[6] the infrared spectrum of the complex isolated after the transfer-hydrogenation reaction, while being identical with that of the complex obtained by heating $RhCl(PPh_3)_3$ in dioxane, is different from that of the complex isolated from a refluxing solution of $RhCl(PPh_3)_3$ in toluene. However, we find that all the additional peaks present occur at the same position (±5 cm^{-1}) as those found in the spectrum of free dioxane. The two peaks at 870 and 890 cm^{-1}, previously attributed[6] to coordinated dioxane, are present at exactly the same position in the spectrum of free dioxane and do not, therefore, constitute evidence of coordination. Moreover, the far-infrared (500-200 cm^{-1}) spectrum of A, apart from a band at 275 cm^{-1} (also present in the spectrum of free dioxane), is identical with that of $Rh_2Cl_2(PPh_3)_4$, having a band at 303 cm^{-1}, attributed to the bridging chloro ligands.[30] Furthermore we find that the ratio of dioxane to rhodium in the complex (A) obtained from a dioxane solution of $RhCl(PPh_3)_3$ after reflux is not constant but varies depending on the time the complex is dried in vacuo. We were unable to obtain meaningful ^1H NMR spectra from the orange-red crystals isolated from the transfer-hydrogenation reaction mixture (catalyst $RhCl(PPh_3)_3$) on cooling to room temperature. In our hands this complex, which on the basis of the above evidence we believe to be solvated $[RhCl(PPh_3)_2]_2$, was virtually insoluble in $CDCl_3$ in the absence of air. We would, however, emphasize the finding of Wilkinson et al.[29] that the dimer is unstable towards oxygen and point out that on exposure to air a suspension of $[RhCl(PPh_3)_2]_2$ in $CDCl_3$ turned into a homogeneous solution, which is possibly due to the formation of the oxygen-bridged dimer $Rh_2(O_2)_2Cl_2(PPh_3)_4$.[31]

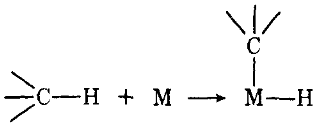
Discussion

One of the fundamental differences between the rhodium-catalyzed transfer hydrogenation discussed above and the corresponding rhodium-catalyzed reduction of olefins by molecular hydrogen is the presence of gaseous hydrogen.[32] Whereas hydrogenation involves the formation of two saturated C-H bonds at the expense of an H-H bond, transfer hydrogenation implies the formation of two saturated C–H bonds at the expense of two saturated C–H bonds. Thus, whereas in hydrogenation one of the essential steps is oxidative addition of the hydrogen to the metal center to give a dihydride species:



$$H_2 + M \longrightarrow \overset{H}{\overset{|}{M}}\text{—}H$$

the analogous step in transfer hydrogenation is oxidative addition of a saturated C–H bond with formation of a hydrido-alkyl species:



Furthermore, in contrast to hydrogenation, in transfer hydrogenation there is no change in overall unsaturation in the system, i.e.

"alkane(1)" + alkene(1) → alkene(2) + "alkane(2)"

These differences allow us to explain the limited scope (cf. results in Table VI) of the transfer-hydrogenation reaction. Not only must the hydrogen donor, "alkane(1)", be capable of interacting productively with the metal center but it must also be able to compete successfully with alkene(1) for the vacant catalyst sites. Furthermore, its dehydrogenation product, alkene(2), should, once formed, leave the catalyst in favor of the chosen hydrogen acceptor, alkene(1). Of the potential hydrogen donors tested only 1,4-dioxane proved capable of meeting these stringent requirements. As is evidenced by the results in Table V, the demands made of the hydrogen acceptor, alkene(1), are much less severe. Most of the olefins tested proved suitable, with only slight differences in activity. The results obtained using substituted styrenes, Table V, show that electronic factors are of limited importance with respect to the hydrogen acceptor in the transfer-hydrogenation reaction. The low activity of ethylene is not surprising as it is known that, compared to propylene and the higher olefins, it forms strong bonds with rhodium.[9,33] Thus it will compete with dioxane more effectively than the other olefins for the vacant sites on the rhodium, thereby causing a decrease in the observed rate of hydrogen transfer. We suggest that the decrease in activity observed with cyclooctene, cyclodecene, and cyclododecene is due to their size—and, hence, poor bonding ability—preventing them from competing successfully with product dioxene for coordination sites.

The increase in catalytic activity resulting from the use of more basic tertiary phosphine ligands (Table II) is in agreement with metal insertion into a C–H bond of the dioxane being the rate-determining process. Although electronic effects in such insertion reactions are poorly understood it has been found,[34] in a number of internal-metalation reactions, that increasing the electron density at the metal center increases the rate of metal insertion into a C–H bond. An analogous rationale may be used for the increase in activity observed on replacing the chloride ligands in $RhCl(PPh_3)_3$ by bromide. With respect to this halogen substitution an analogous activity trend is found[35] in the hydrogenation reaction. The behavior of the mixed arylalkyl- and trialkylphosphine complexes is, however, diametrically opposed to that observed[7] in the rhodium-catalyzed hydrogenation. There it is found that complexes comprizing triethyl- or diethylphenylphosphine ligands are virtually inactive as catalysts. Further evidence for the occurrence of C–H bond rupture in the rate-determining process is provided, as previously suggested,[6] by the large, ca. 3, kinetic isotope effect.

Thus, in agreement with Nishiguchi and Fukuzumi, we consider that the essential rate-determining process involves oxidative-addition of a dioxane C–H bond to the rhodium to form a monohydrido complex $RhClH(C_4H_7O_2)(PPh_3)_2S'$ (S′ = dioxane or olefin). Nishiguchi et al.[6] propose, by analogy with rhodium-catalyzed hydrogenation, that the following step is the formation of the dihydrido complex $RhClH_2(PPh_3)_2$ or $RhClH_2(PPh_3)_2S'$. Although it seems probable that a relation exists between rhodium-catalyzed hydrogenation, involving molecular hydrogen, and transfer hydrogenation care should be exercised in drawing conclusions based on this relationship, especially with respect to possible reaction intermediates. The proven[8] existence of a dihydrido intermediate in rhodium-catalyzed hydrogenation does not, in our opinion, imply the occurrence of a similar intermediate in transfer hydrogenation. An alternative sequence would involve the intermediacy of a dialkylrhodium species, $RhCl(C_5H_9)(C_4H_7O_2)(PPh_3)_2$, formed by attack of the cyclopentene on the monohydrido species. This would imply that the transfer of hydrogen from dioxene to cyclopentene is a stepwise process. We have been unable to distinguish, experimentally, between these two alternatives.

The observation that during the course of the transfer-hydrogenation reaction the organic groups of the tertiary-phosphine ligands interact directly with the metal center is of some significance. Tertiary phosphine ligands are extensively used to modify the properties of transition metal catalysts in a wide range of catalytic reactions[36] and, as previously pointed out,[5] it has generally been assumed that, with the possible exception of arylphosphine complexes,[37] the organic groups attached to the phosphorus undergo no direct interaction with the metal center.

We would suggest that the apparent first-order dependence on cyclopentene may be explained in terms of competing reversible complex formation between the catalytic species and both cyclopentene and product dioxene.[38] The basic reaction scheme then includes (a) a reversible complex formation between the catalytic species, M, and cyclopentene, C, (b) a reversible inhibition by the coproduct dioxene, P, and (c) the reaction of the cyclopentene-catalyst complex with the dioxane (d) to give dioxene and cyclopentane (CH_2).[39]

$$M + C \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} MC \tag{a}$$

$$M + P \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} MP \tag{b}$$

$$MC + D \xrightarrow{k_3} M + P + CH_2 \tag{c}$$

The observation that either increasing the initial concentration of cyclopentene or adding product dioxene to the reaction mixture causes a decrease in the observed first-order rate constant is in agreement with this concept of competing reversible complex formation.

Assuming that the initial dioxene concentration is zero and following the treatment detailed by Zajacek et al.,[40] we can obtain a theoretical rate equation of the form

$$-\frac{d[C]}{dt} = \frac{k_3[D][M]_0}{(K_C/[C]) + K_P K_C([C]_0/[C]) + (1 - K_C K_P)} \tag{2}$$

where $K_C = (k_{-1} + k_3[D])/k_1$ and $K_P = [MP]/[M][P]$.

The experimental observation of apparent first-order dependence of the rate of transfer-hydrogenation on cyclopentene implies that the term $1 - K_CK_P$ must be negligible relative to the remaining terms in the denominator; elimination of this term from (2) gives

$$-\frac{d[C]}{dt} = \frac{k_3[D][M]_0[C]}{K_C + K_CK_P[C]_0} \tag{3}$$

an equation which is consistent with the apparent first-order dependence on cyclopentene. Rearrangement of (3), using the experimental fact that

$$-\frac{d[C]}{dt} = k_{obsd}[C]$$

gives

$$k^{-1}{}_{obsd} = \frac{K_C}{k_3[D][M]_0} + \frac{K_CK_P[C]_0}{k_3[D][M]_0} \tag{4}$$

implying that a plot of $k^{-1}{}_{obsd}$ vs. $[C]_0$ should be linear. This is found to be the case as shown in Figure 2. In principle eq 4 provides a means of estimating K_P, the equilibrium constant for the catalyst–dioxene complex, since the slope of the lines in Figure 2 divided by the respective intercepts should give values of K_P for the two-catalyst systems. The line for the Rh_2Cl_2(cyclooctene)$_4$–4PEt$_3$ catalyst passes, within experimental error, through (very close to) the origin, indicating that $K_C < k_3[D][M]_0$, i.e., that equilibrium a lies predominantly to the right. Similarly, since the term $(1 - K_PK_C)$ must be negligible compared to the other terms in the denominator of eq 2 and since in terms of the proposed mechanism this implies that K_P must be approximately the inverse of K_C, equilibrium b also lies to the right. Unfortunately, due to the experimental errors involved, we are unable to obtain a meaningful value for K_P from Figure 2. Extrapolation of the line obtained for the $RhCl(PPh_3)_3$, labeled B in Figure 2, results in a negative intercept on the ordinate axis. We have no satisfactory explanation for this result. Equation 4 clearly requires a positive intercept; we can only suggest that the actual reaction is more complicated than the relatively simple system represented by eq a, b, and c or that the negative intercept reflects some unforeseen experimental error involved in the measurement of the rate constants.[41] We have experienced some difficulty in obtaining reproducible kinetic data for the $RhCl(PPh_3)_3$ system; we observed considerable variation in k_{obsd} (sometimes of the order of 15%) in going from one catalyst batch to another.[42] Other workers have encountered similar problems in obtaining accurate and reproducible kinetic data for the corresponding $RhCl(PPh_3)_3$-catalyzed hydrogenation of olefins; there it was suggested that trace amounts of peroxides in the olefin, contamination of the catalyst by rhodium(II) species, or the presence of small quantities of oxygen could affect the rate of hydrogenation in an unpredictable manner.[43] The inability to obtain reliable values for K_P and K_C unfortunately precludes a meaningful determination of the activation parameters. The observation that the found order in rhodium complex is slightly less than one may be due to some of the rhodium being present, under the reaction conditions, i.e., at temperature >150 °C, as the chloro-bridged dimer. It has recently been shown[44] that for $RhClL_3$, where L = tri-*p*-tolylphosphine, dimer formation is enhanced by raising the temperature.

Experimental Section

All of the complexes used in this study were prepared as previously reported (references given in Table IV and the text).

Compounds and solutions were prepared and handled under an argon atmosphere in Vacuum Atmosphere, Inc., dryboxes. Infrared spectra were recorded on either a Perkin-Elmer 457 spectrometer (4000–400 cm^{-1}; KBr disk) or a Perkin-Elmer 225 spectrometer (500–200 cm^{-1}; CsI disk).

Both the 1,4-dioxane and the cyclopentene were rigorously purified prior to use by distillation from sodium.[45] They were kept under an argon atmosphere at all times.

The transfer-hydrogenation reactions were carried out in glass ampoules, sealed under argon and vibrated (Vibromixer) in an oil bath at a given constant (±1 °C) temperature for the required time. Unless otherwise stated the solutions remained homogeneous throughout the reaction. The catalyst containing triethylphosphine was prepared in situ by adding triethylphosphine (4 molar equiv) to bis(cyclooctene)chlororhodium(I) dimer in dioxane under argon. After reaction the cyclopentene and cyclopentane were separated by gas–liquid chromatography (12-ft Carbowax 20 M column at 40 °C using a Hewlett-Packard 5750 G gas chromatograph) and the percentage conversion was calculated. This was found to correspond (±5%) to the conversion of dioxane to dioxene measured by ^{1}H NMR spectroscopy.

Below we describe in detail two examples of the transfer-hydrogenation reaction: (a) with Rh_2Cl_2(cyclooctene)$_4$-4PEt$_3$, and (b) with $RhCl(PPh_3)_3$ as the catalyst.

(a) Rh_2Cl_2(cyclooctene)$_4$-4PEt$_3$ Catalyst System. Rh_2Cl_2(cyclooctene)$_4$ (0.072 g, 0.1 mmol) was placed in a 20-ml Pyrex-glass ampoule. After degassing, the ampoule containing the complex was transferred to an argon-filled drybox in which 1,4-dioxane (10 ml), cyclopentene (0.425 ml, 4.84 mmol), and triethylphosphine (0.060 ml, 0.45 mmol) were added. The ampoule was stoppered and removed from the drybox. While taking extreme care to maintain an argon atmosphere the ampoule was cooled to −80 °C and sealed. After allowing the sealed ampoule to attain room temperature, and ensuring that the reaction mixture was homogeneous, the ampoule was vibrated (vibromixer) in a thermostated oil bath at the required temperature (±1 °C) for the required time. The reaction time quoted refers to the time the ampoule was in the oil bath; no correction was made for the time required for the reaction mixture to attain the temperature of the oil bath.[23] After reaction the ampoule was removed from the bath and immediately placed in a freezer at −30 °C. When the ampoule had reached room temperature, it was opened and the reaction mixture analyzed by gas-liquid chromatography as previously detailed.

(b) $RhCl(PPh_3)_3$ Catalyst System. $RhCl(PPh_3)_3$ (0.185 g, 0.2 mmol) was placed in a 20-ml Pyrex-glass ampoule. After degassing, the ampoule containing the complex was transferred to an argon-filled drybox in which dioxane (10 ml) and cyclopentene (0.439 ml, 5.0 mmol) were added. After this the procedure adopted was as detailed above for the Rh_2Cl_2(cyclooctene)$_4$-4PEt$_3$ system.

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(24) R. Nishiguchi and K. Fukuzumi report[8] that, with $RhCl(PPh_3)_3$ as the catalyst, the transfer-hydrogenation reaction is zero-order in cyclopentene. We have *been unable to reproduce* this *result*.

(25) Nishiguchi et al. report that in the region where the catalyst concentration is higher than 0.003 M the rate might be regarded as having pseudo-first-order dependence on the catalyst concentration.

(26) T. Nishiguchi and K. Fukuzumi state[6] that, whereas toluene is a suitable cosolvent, benzene strongly inhibits the transfer-hydrogenation reaction. *We have been unable to reproduce* this *surprising result*; in fact, we found that addition of 0.5 M benzene to the reaction mixture (reported[6] to depress the rate of reduction of cyclopentene to ca. one-eighth) *had little effect on the reaction rate:* k_{obsd} (absence of benzene) $= 2.4 \pm 0.2\ 10^{-4}\ s^{-1}$; k_{obsd} (addition of 0.5 M benzene) $= 2.1 \pm 0.2 \times 10^{-4}\ s^{-1}$.

(27) T. Nishiguchi and K. Fukuzumi report[6] a value of 21.6 kcal mol^{-1} (no error quoted).

(28) Using diphenylethylphosphine in place of triethylphosphine in the catalyst system we obtain a value of 2.9 ± 0.5 for the kinetic isotope effect at 180 °C. Nishiguchi et al.[6] report a value of 3.1 with $RhCl(PPh_3)_3$ as the catalyst.

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(38) Analogous kinetic behavior has been observed by Zajacek et al.[40] in the molybdenum-catalyzed epoxidation of 1-octene by organic hydroperoxides.

(39) An alternative scheme, viz.

$$\begin{gathered} D + M \rightleftharpoons MD \\ MD + C \rightleftharpoons MDC \\ MD + P \rightleftharpoons MDP \\ MDC \rightarrow M + P + CH_2 \end{gathered}$$

involving prior coordination of dioxane to the catalytic species would, clearly, give the same kinetic results.

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(41) An analogous treatment of the data presented in Table VIII also provides, in principle, a method of obtaining a value of K_p, i.e., a plot of ${k_{obsd}}^{-1}$ vs. $[C]_0 + [P]_0$ being linear (see Figure 3, ${k_{obsd}}^{-1}$ vs. $[P]_0$) and division of the slope by the intercept giving K_p. However, although in this case both intercepts are positive, 504 ± 206 and 205 ± 373 for catalysts A and B, respectively, the errors involved preclude a meaningful value of K_p being obtained. Qualitatively the discussion is similar to that of the $Rh_2Cl_2(cyclooctene)_4{-}4PEt_3$ data shown in Figure 2.

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The Catalytic Reduction of Nitric Oxide by Carbon Monoxide Using Dichlorodicarbonylrhodium(I) Anion

Carol D. Meyer and Richard Eisenberg*

Contribution from the Department of Chemistry, University of Rochester,
Rochester, New York 14627.

Received March 31, 1975

Abstract: The catalytic reduction of nitric oxide by carbon monoxide to yield N_2O and CO_2 has been studied at 23°C using $[RhCl_2(CO)_2]^-$ as the catalyst. When solutions of the rhodium carbonyl anion in aqueous acidic ethanol are placed under a mixed gas atmosphere of NO and CO (4:3 ratio), a green color develops characteristic of an unstable intermediate and product evolution is observed by GC analysis. Quantitative recovery of $[RhCl_2(CO)_2]^-$ at the end of the catalytic runs and recharging of the rhodium carbonyl anion solutions with no loss of activity indicate the true catalytic behavior of this system. It is also found that H_3O^+ is a necessary cocatalyst for this reaction. The green catalytic intermediate is proposed as a dinitrosylcarbonyl and a mechanism for the catalytic cycle is presented. Studies using $RhCl_3$ solutions establish that reduction of Rh(III) to $[RhCl_2(CO)_2]^-$ is a necessary prerequisite to the onset of catalytic activity under NO/CO atmospheres.

The catalytic reduction of nitric oxide by carbon monoxide possesses both intrinsic interest and environmental importance. The former arises from the extensive bond reorganizations implicit in reactions 1 and 2 including the oxygen atom transfers required by their stoichiometries.

$$2NO + 2CO \rightarrow N_2 + 2CO_2 \qquad (1)$$

$$2NO + CO \rightarrow N_2O + CO_2 \qquad (2)$$

The environmental importance results from the presence of both NO and CO in most combustion exhausts and the need to convert these compounds into less harmful chemical entities.

While reactions 1 and 2 are overwhelmingly favored thermodynamically, they do not proceed at appreciable rates in the absence of a catalyst. To date, most studies of the catalyzed reduction of nitric oxide by carbon monoxide have employed heterogeneous catalysts, usually metals and metal oxides, at elevated reaction temperatures.[1] The use of metal complexes in solution as catalysts for reactions of this type has only recently begun to be explored. In 1973 Johnson and Bhaduri[2] reported that the dinitrosyl $[Ir(NO)_2(PPh_3)_2]^+$ reacts with carbon monoxide according to eq 3, and conversion of the cationic tricarbonyl complex $[Ir(CO)_3(PPh_3)_2]^+$ back to the reactant dinitrosyl suggested the possibility of a continuous cycle for reaction 2. Catalysis of eq 2 by such dinitrosyl complexes has subsequently been reported by Haymore and Ibers.[3]

$$Ir(NO)_2L_2^+ + 4CO \rightarrow Ir(CO)_3L_2^+ + N_2O + CO_2 \qquad (3)$$