crystallized from methanol: mp 99.5–100.0°; ir ($CHCl_3$) 2.80, 3.29, 3.35, 3.50, 6.93, 7.07, 7.28, 7.83, 8.08, 8.72, and 9.25 μ; nmr ($CDCl_3$) 7.95 (s, 2-dithiane CH_3), 8.21 (s, CH_3), 6.6 (s, OH). *Anal.* Calcd for $C_{12}H_{22}OS_4$: C, 46.45; H, 7.17; O, 5.16; S, 41.25. Found: C, 46.51; H, 6.93; O, 5.31; S, 41.11.

(6) 2-Hexahydrobenzoyl-2-methyl-1,3-dithiane (20, R = CH_3, R′ = C_6H_{11}) from 5, R = CH_3, and Cyclohexane Carboxylic Ester. A solution of 17.0 mmol of the lithium compound was added dropwise within 12 min at −60° to 1.37 g (8.8 mmol) of the ethyl ester in 15 ml of THF. The bath temperature was allowed to warm to −10° within 70 min and the mixture was kept 1 day in a refrigerator. The usual work-up with chloroform and distillation (200° (0.1 mm)) gave 60% of a colorless oil: ir (neat) 3.35, 5.87, 6.92, 7.33, 9.36, and 10.13 μ; nmr (CCl_4) 2.25 (s, 2-dithiane CH_3).

(7) Bis(1,3-propylenedithioacetal) of 3-hydroxy-3-phenylpentane-2,4-dione (22, R = CH_3, R′ = C_6H_5) from 5, R = CH_3, and Ethyl Benzoate. Neat ester (388 mg, 2.58 mmol) was added to a solution of 5.64 mmol of metalated 2-methyl-1,3-dithiane at 0°. After removing the ice bath stirring was continued for 1 hr. Work-up with chloroform–water gave rise to 931 mg (96.6%) of product **22** as colorless crystals, mp 151–155°. The analytical sample was prepared by recrystallization from CH_3OH–$CHCl_3$ 3:1: mp 156.5–158.0°; ir ($CHCl_3$) 2.84, 3.20, 3.28, 3.35, 3.49, 6.70, 6.92, 7.07, 7.28, 7.83, 8.60, 9.31, 9.74, and 14.2 μ; nmr ($CDCl_3$) 7.85 (s, CH_3), 5.58 (s, OH), 2.0 (broad m, C_6H_5), and 2.7 (narrow m, C_6H_5). *Anal.* Calcd for $C_{17}H_{24}OS_4$: C, 54.83; H, 6.50; O, 4.29; S, 34.38. Found: C, 54.72; H, 6.55; O, 4.41; S, 34.12.

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Registry No.—**5** (R = $(C_2H_5O)_2CHCH_2$), 53178-53-3; **6** (R = *t*-C_4H_9), 6007-21-2; **6** (R = cyclohexen-1-yl-4), 53178-49-7; **6** (R = H), 505-23-7; **6** (R = 1-chlorocyclohexyl-1), 53178-50-0; **15**, 53178-54-4; **17**, 53209-81-7; **18** (R′ = C_6H_5, R″ = H), 17590-58-8; **18** (R′ = R″ = C_6H_5), 36998-40-0; **18** (R′ = R″ = $(CH_2)_5$), 37891-71-7; **19**, 5849-28-5; **20** (R = H, R′= OH), 20461-89-6; **20** (R = CH_3, R′ = OH), 4901-19-3; **20** (R = *t*-C_4H_9, R′ = OH), 4882-94-4; **20** (R = H, R′ = OC_2H_5), 20462-00-4; **20** (R = H, R′ = styryl), 4883-02-7; **20** (R = CH_3, R′ = H), 4882-97-7; **20** (R = CH_3, R′ = H) DNPH, 5849-01-4; **20** (R = CH_3, R′ = OEt), 4882-95-5; **20** (R = R′ = CH_3), 5011-99-4; **20** (R = R′ = CH_3) DNPH, 53178-55-5; **20** (R = CH_3, R′ = C_6H_{11}), 4882-98-8; **22** (R = H, R′ = styryl), 4883-03-8; **22** (R = R′ = CH_3), 4882-99-9; **22** (R = CH_3, R′ = C_6H_5), 4883-00-5; propane-1,3-dithiol, 109-80-8; propionaldehyde, 123-38-6; hexanal, 66-25-1; pivalaldehyde, 630-19-3; methyl glyoxal bis(1,3-propylene)dithioacetal, 53178-56-6; cyclohexene-1-carboxyaldehyde-4, 100-50-5; benzalanilide, 93-98-1; ethyl chloroformate, 541-41-3; ethyl cinnamate, 103-36-6; dimethylformamide, 68-12-2; epichlorohydrin, 106-89-8; acetyl chloride, 75-36-5; ethyl cyclohexanecarboxylate, 3289-28-9; ethyl benzoate, 93-89-0.

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Transfer Hydrogenation and Transfer Hydrogenolysis. V. Hydrogen Transfer from Amines, Ethers, Alcohols, and Hydroaromatic Compounds to Olefins Catalyzed by Chlorotris(triphenylphosphine)rhodium(I)

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In the hydrogen transfer from organic compounds to olefins catalyzed by $RhCl(PPh_3)_3$, some cyclic amines were found much more reactive than oxygenated and hydroaromatic compounds such as primary and secondary alcohols, tetralin, etc. Reactivity decreased in the order indoline > pyrrolidine > tetrahydroquinoline > piperidine > 2,3-butanediol > dioxane > cyclohexanol > isopropyl alcohol. Indoline and tetrahydroquinoline gave stoichiometrically indole and quinoline, respectively.

The transfer of hydrogen to olefins from hydroaromatic compounds and primary and secondary alcohols[2] is heterogeneously catalyzed. Alcohols,[3] arylaldehydes,[4] *N*-methylformamide,[4] formic acid,[4] and dioxane[5] have been reported as hydrogen sources in homogeneous reactions.

This paper reports on investigation of the hydrogen-donating ability of various organic compounds catalyzed by chlorotris(triphenylphosphine)rhodium(I), which has high catalytic activity in the reduction of olefins by molecular hydrogen.[6] It was found that some cyclic amines such as

Table I
Transfer Hydrogenation of Cycloheptene[a]

Hydrogen donor and solvent	Registry No.	Yield of cycloheptane, %	Dehydrogenation product
Tetralin	119-64-2	60	*Naphthalene*
Cyclohexene[b]	110-83-8	2	
Tetradecane[d]	629-59-4	2	
Cyclohexanol	108-93-0	100	Cyclohexanone
2,3-Butanediol	513-85-9	100	
Isopropyl alcohol	67-63-0	92	Acetone
sec-Butyl alcohol	78-92-2	72	2-Butanone
1,3-Butanediol[c]	107-88-0	37	
Benzyl alcohol[c]	100-51-6	12	
Isobutyl alcohol[c]	78-83-1	7	
Ethyl alcohol[c]	64-17-5	6	
Propyl alcohol[c]	71-23-8	6	
Butyl alcohol[c]	71-36-3	6	
Ethylene glycol[c]	107-21-1	5	
tert-Butyl alcohol[d]	75-65-0	3	
Dioxane	123-91-1	72	Dioxene
Tetrahydrofuran	109-99-9	22	
Tetrahydropyran[c]	142-68-7	8	
Isopropyl ether[d]	108-20-3	4	
2,3-Dihydrofuran	1191-99-7	2	
2,3-Dihydropyran[c]	110-87-2	2	
Propyl ether[d]	111-43-3	1	
Propionic acid butyl ester	590-01-2	7	
Acetone	67-64-1	7	
Acetic acid[c]	64-19-7	3	
Acetic acid benzyl ester	140-11-4	3	
2-Butanone	78-93-3	3	
Tetrahydrothiophene	110-01-0	3	

[a] Cycloheptene (0.50 *M*) and $RhCl(PPh_3)_3$ (0.02 *M*) were heated at 190° for 1 hr in the designated organic compound which was used as a hydrogen donor and solvent. [b] Cyclopentene was used instead of cycloheptene. [c] The formation of $RhCl(CO)(PPh_3)_2$ was observed. [d] The catalyst did not dissolve completely even at 190°.

pyrrolidine, piperidine, indoline, and tetrahydroquinoline were much better donors than hydrocarbons, ethers, carbonyl compounds, and most alcohols studied.

Results and Discussion

Hydrogen-Donating Ability of Hydrocarbons and Oxygen Compounds. The hydrogen-donating ability of some hydrocarbons and oxygen compounds was evaluated by heating them with cycloheptene and $RhCl(PPh_3)_3$. The dehydrogenation products identified and the yields of cycloheptane are shown in Table I. It has been reported that cyclohexene hydrogenates several olefins in the presence of palladium.[1a] However, cyclohexene hardly reduced cycloheptene in this system, and the hydrogen-donating ability of tetralin was found much higher than that of cyclohexene.

Secondary alcohols and dioxane had high hydrogen-donating ability and stoichiometrically gave the corresponding ketones and dioxene, respectively. For example, when an isopropyl alcohol solution of cycloheptene (0.50 *M*) and $RhCl(PPh_3)_3$ (0.02 *M*) was heated at 170° for 1 hr, the formation of 0.34 *M* acetone and 0.36 *M* cycloheptane in addition to the survival of 0.14 *M* cycloheptene was shown by the glc analysis of the reaction mixture. Also a dioxane solution of cycloheptene (0.50 *M*) and the catalyst, which had been heated at 190° for 1 hr, contained 0.35 *M* dioxene and 0.35 *M* cycloheptane as well as 0.14 *M* cycloheptene. The cyclic ether, tetrahydrofuran which contains one oxygen atom, also reduced the olefin. When primary alcohols, tetrahydropyran, and 2,3-dihydropyran were used, reduction of the olefin hardly occurred and $RhCl(CO)(PPh_3)_2$ was obtained as yellow crystals. This carbonyl complex does not catalyze the transfer hydrogenation of cyclopentene to cyclopentane by dioxane.[5] Therefore, $RhCl(PPh_3)_3$ is inferred to be deactivated by carbonyl abstraction from primary alcohols or pyrans. Moreover, the inference is supported by the fact that primary alcohols reduce olefins effectively to form the corresponding aldehydes in the presence of $RhH(PPh_3)_4$,[3e] and $RhCl(PPh_3)_3$ abstracts carbon monoxide from aldehydes to give $RhCl(CO)(PPh_3)_2$.[6,7] When *N*-methylformamide or formic acid was used, facile formation of the carbonyl complex was observed.

Hydrogen scarcely transferred from tetrahydrothiophene.

Table II
Hydrogen Transfer from Amines to Cycloheptene[a]

Hydrogen donor and solvent		Yield of cycloheptane %
Indoline	496-15-1	100
Pyrrolidine	123-75-1	100
Tetrahydroquinoline	635-46-1	98
Piperidine	110-89-4	94
Morpholine	110-91-8	44
N-Methylmorpholine	109-02-4	40
Benzylamine	100-46-9	26
Piperazine	110-85-0	23
Isopropylamine	75-31-0	18
N-Methylpiperazine	109-01-3	17
N-Methylpyrrolidine	120-94-5	12
Propylamine	107-10-8	8
N-Methylpiperidine	626-67-5	7
N,N'-Dimethylpiperazine	106-58-1	6
Dipropylamine[b]	142-84-7	3
Tripropylamine[b,c]	102-69-2	2

[a] Cycloheptene (0.50 *M*) and $RhCl(PPh_3)_3$ (0.02 *M*) were heated at 190° for 1 hr in the designated amine which was used as a hydrogen donor and solvent. [b] Cyclopentene was used instead of cycloheptene. [c] The catalyst did not dissolve completely even at 190°.

Table III
Quantitative Relation in Transfer Hydrogenation[a]

Hydrogen donor	Donor concn, *M*	Temp, °C	Time, hr	Composition of reaction mixture, *M*: Cycloheptane	Cycloheptene	Dehydrogenation product	Survived donor
Indoline[b]	0.50	170	1	0.34	0.16	0.34[c]	0.15
Tetrahydroquinoline	0.50	190	2	0.46	0.05	0.23[d]	0.26
Piperidine[e]	0.25	180	2	0.15	0.34	*f*	0.10
Pyrrolidine[e]	0.25	180	1	0.22	0.29	*g*	*h*

[a] Cycloheptene (0.50 *M*), $RhCl(PPh_3)_3$ (0.02 *M*), and the designated hydrogen donor were heated in toluene. [b] The concentration of the catalyst was 0.01 *M*. [c] Indole was formed. [d] Quinoline was formed. [e] *o*-Dichlorobenzene was used as a solvent. [f] Pyridine was not detected. [g] Neither pyrrole nor 3-pyrroline was detected. [h] Pyrrolidine was detected, but the amount could not be measured.

Hydrogen-Donating Ability of Amines. Amines cannot poison $RhCl(PPh_3)_3$ by carbonylation and also coordinate well. So they were expected to be excellent hydrogen donors and the results are shown in Table II. N-Unsubstituted cyclic amines such as pyrrolidine, piperidine, indoline, and tetrahydroquinoline had greater hydrogen-donating ability than dioxane and most alcohols but alicyclic

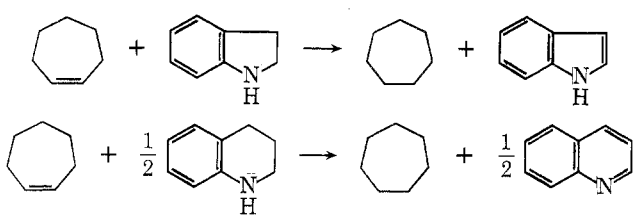
Table IV
Solvent Effect in Transfer Hydrogenation[a]

Solvent	Registry No.	Initial rate, mol l.$^{-1}$ min^{-1}
Chlorobenzene	108-90-7	6.3×10^{-3}
o-Dichlorobenzene	95-50-1	5.1×10^{-3}
Aniline	62-53-3	4.0×10^{-3}
Anisole	100-66-3	3.4×10^{-3}
Toluene	108-88-3	2.9×10^{-3}
Benzene	71-43-2	2.7×10^{-3}
2-Butanone		2.3×10^{-3}
Dimethyl sulfoxide	67-68-5	1.1×10^{-3}
Pyridine	110-86-1	1.6×10^{-4}
Propionitrile	107-12-0	1.1×10^{-4}

[a] Cyclopentene (0.50 *M*), indoline (0.50 *M*), and $RhCl(PPh_3)_3$ (0.006 *M*) were heated at 160° in the designated solvent.

amines were less effective. For example, the conversions of cyclopentene to cyclopentane were 100% in the reaction in pyrrolidine at 150° for 1 hr and 29% at 120°, while the corresponding values for dioxane were 22 and 1%, respectively. N-Substituted cyclic amines such as *N*-methylpyrrolidine and *N*-methylpiperidine showed much smaller hydrogen-donating ability than the corresponding N-unsubstituted ones. However, morpholine and *N*-methylmorpholine showed comparable ability.

Analyses of the dehydrogenation products are summarized in Table III. It is clearly shown from the observations described below that indoline and tetrahydroquinoline donated hydrogen to cycloheptene stoichiometrically, to form indole and quinoline, respectively, as follows.



(1) The amount of indole was equal to that of cycloheptane and the amount of quinoline was equal to one-half the amount of cycloheptane. (2) The total amount of the survived hydrogen donor and the dehydrogenated donor equaled that of the charged hydrogen donor. (3) The total amount of cycloheptane and cyclohetene was equal to that of the charged cycloheptene. (4) In the absence of the hydrogen sources, cycloheptene was not reduced in toluene. (5) Cycloheptadienes which are the products of the disproportionation of the olefin, were negligibly detected.

The amount of piperidine consumed was almost equal to that of the cyclopentane formed but no low-boiling dehydrogenation products such as pyridine were detected. This suggests that the dehydrogenation intermediates from piperidine formed products of higher molecular weight. The amount of the survived pyrrolidine could not be measured precisely and anticipated five-membered dehydrogenation products such as pyrrole and 3-pyrroline were not detected. It has been reported that 1-piperideine and 1-pyrroline are so unstable as to undergo rapid trimerization in the absence of amines[8] or addition reaction in the presence of amines.[9] Therefore, it is inferred that dehydrogenation intermediates might react further to give products of high-boiling points which could not be detected by glc analysis.

The driving force for piperidine and pyrrolidine to donate hydrogen may not be due to aromatization, because aromatization products, such as pyridine and pyrrole, were not detected in the reaction mixtures.

Table V
Rate of Transfer Hydrogenation of Cycloolefins[a]

Cycloolefin (0.30*M*)	Registry No.	Initial rate, mol l.$^{-1}$ min^{-1} $\times 10^3$
Cyclopentene	142-29-0	2.6
Cyclohexene	110-83-8	2.8
Cycloheptene	628-92-2	2.8
Cyclooctene	931-88-4	1.8
1,3-Cyclooctadiene	1700-10-3	0
1,5-Cyclooctadiene	111-78-4	0[b]

[a] Cycloolefin, indoline (0.25 *M*), and $RhCl(PPh_3)_3$ (0.006 *M*) were heated at 160° in xylene. [b] 1,5-Cyclooctadiene was partly isomerized to 1,3- and 1,4-dienes.

Table VI
Ability to Donate Hydrogen[a]

Hydrogen donor	Initial rate, mol l.$^{-1}$ min^{-1}
None	0
Indoline	4.8×10^{-3}
Pyrrolidine	1.9×10^{-3}
Tetrahydroquinoline	1.4×10^{-3}
Piperidine	2.8×10^{-4}
2,3-Butanediol	1.5×10^{-4}
Dioxane	6.1×10^{-5}
Cyclohexanol	5.7×10^{-5}
Isopropyl alcohol	3.5×10^{-5}

[a] Cyclopentene (0.50 *M*), a hydrogen donor (0.50 *M*), and $RhCl(PPh_3)_3$ (0.006 *M*) were heated in toluene at 160°.

Measurement of Reaction Rates. The initial rates of the reduction of several olefins were measured in several solvents. The conversion of cyclomonoenes to cycloparaffins was proportional to reaction time over the ranges up to 20–25% conversion. Initial rates were derived from the linear parts.

Initial rates of the reaction of cyclopentene with indoline were measured in several solvents, and the results are summarized in Table IV. Some solvents which have high polarity and strong coordinating power, such as dimethyl sulfoxide, pyridine, and propionitrile, dissolved the catalyst easily, but reduction in these solvents was slow. Possibly strongly coordinating solvents block coordination of reactants. In most aromatic solvents such as halogenated benzenes and toluene, the catalyst dissolved well at reaction temperatures and the reaction proceeded rapidly. Toluene or xylene was employed in the reactions described hereafter because of the convenience of the glc analysis.

The initial rates of transfer hydrogenation of several cycloolefins by indoline are shown in Table V. There is little difference among the rates of the cyclomonoenes except for cyclooctene. Although partial isomerization of 1,5-cyclooctadiene to 1,3-cyclooctadiene occurred, the cyclooctadienes were not reduced. Inertness of the cyclooctadienes toward reduction by molecular hydrogen has also been reported[10] and may be rationalized by their strong coordination power[11] which like in the case of excess triphenylphosphine saturates the catalyst.[6] The reason why cyclooctene was reduced more slowly than other cyclomonoenes may be that it was contaminated with 0.5% of 1,5-cyclooctadiene.

The rates of the reduction of cyclopentene in toluene were measured in the presence of several hydrogen donors. From the results summarized in Table VI, it was found that the hydrogen-donating ability decreased in the order: indoline > pyrrolidine > tetrahydroquinoline > piperidine > 2,3-butanediol > dioxane > cyclohexanol > isopropyl alcohol.

Experimental Section

Materials. $RhCl(PPh_3)_3$[6] and dioxene[12] were prepared by the methods previously reported. Olefins and ethers were purified by distillation over metallic sodium. Alcohols were dried with molecular sieves after distillation. Amines, except for piperadine, were distilled. Piperadine was recrystallized from benzene. Tetralin and all solvents were purified by distillation and dried by usual methods. The compounds corresponding to the dehydrogenation products, excluding dioxene, were purchased and purified by distillation.

Transfer Hydrogenation in Excess Hydrogen Donor. Cycloheptene (48.1 mg, 0.50 mmol) or cyclopentene (34.1 mg, 0.50 mmol) and $RhCl(PPh_3)_3$ (18.5 mg, 0.02 mmol) were put into a Pyrex glass tube which had been sealed at one end. Into the mixture, an organic compound, which serves both as a hydrogen donor and a solvent, was added, and the total volume of the solution was made 1.0 ml. The tube was sealed under vacuum after two freeze–pump–thaw cycles at 10^{-2} Torr on a vacuum line with liquid nitrogen. The sealed tube was heated for 1 hr in the silicone-oil bath kept at 190 ± 1°. The reaction mixture was submitted to glc analysis which was performed at 90° for cycloheptene or at 50° for cyclopentene with Hitachi K 53 equipped with a flame-ionization detector, using 25 μl of cyclohexane as an internal standard. A 2 m × 6 mm stainless steel column packed with 25% of 1,2,3-tris(2′-cyanoethoxy)propane on Celite 545 was used. The detection and identification of dehydrogenation products were tried using various columns.

An Example of Stoichiometric Transfer Hydrogenation in a Solvent. Cycloheptene (48.1 mg, 0.50 mmol), indoline (59.5 mg, 0.50 mmol), and $RhCl(PPh_3)_3$ (9.3 mg, 0.01 mmol) were put into a Pyrex glass tube sealed at one end and the total volume of the solution was made 1.0 ml by the addition of toluene as a solvent. The tube, sealed by the method described above, was heated in a silicone-oil bath kept at 170 ± 1° for 1 hr. Though the catalyst dissolved slowly at room temperature, it dissolved at once at the elevated temperature. The reaction mixture was submitted to glc analysis. The amounts of cycloheptane and cycloheptene were measured using the column described above, and the amounts of indole and indoline were measured using a 1 m × 6 mm stainless steel column packed with 25% of Silicone GE SE-30 on Celite 545. In the latter, *n*-tetradecane was used as an internal standard.

Other transfer hydrogenations were carried out in a similar way.

An Example of Kinetic Runs. Six reaction samples, prepared by the method described above, were heated in the silicone-oil bath kept at 150 ± 1° for 10, 20, 30, 40, 50, and 60 min. The reaction mixtures were submitted to glc analysis.

Registry No.—$RhCl(PPh_3)_3$, 14694-95-2.

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Transfer Hydrogenation and Transfer Hydrogenolysis. VI. The Mechanism of Hydrogen Transfer from Indoline to Cycloheptene Catalyzed by Chlorotris(triphenylphosphine)rhodium(I)

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The mechanism of hydrogen transfer from indoline to cycloheptene in toluene catalyzed by $RhCl(PPh_3)_3$ has been studied. The rate data of the reaction can be accommodated by the rate expression of the form, rate = $a[D][C]_0/(b + [L])$ where $[C]_0$, [D], and [L] are the concentration of the catalyst, indoline, and triphenylphosphine, respectively. The rate-determining step of the reaction is inferred to be the dehydrogenation of indoline, that is, the hydrogen transfer from the amine to a Rh(I) complex to form a hydride complex by oxidative addition.

In the previous paper,[1] we have reported that in hydrogen transfer from organic compounds to olefins catalyzed by $RhCl(PPh_3)_3$, some cyclic amines, such as indoline, pyrrolidine, tetrahydroquinoline, and piperidine, have much higher hydrogen-donating ability than ethers, hydroaromatic compounds, and most alcohols. This study was undertaken to investigate the mechanism of the hydrogen transfer from amines to olefins catalyzed by $RhCl(PPh_3)_3$.

Results and Discussion

Indoline was used as a hydrogen donor because the amine had the highest hydrogen-donating ability and gave the dehydrogenation product, indole, stoichiometrically. Cycloheptene and toluene were used as a hydrogen acceptor and a solvent, respectively.

Dependence on the Catalyst Concentration. It has been reported that $RhCl(PPh_3)_3$ dimerizes to the inactive species, $[RhCl(PPh_3)_2]_2$, during the reduction by molecular hydrogen in benzene and that the rate is expressed in the form: $R = \alpha'[RhCl(PPh_3)_3] - \beta'[RhCl(PPh_3)_3]_2$ in which α' and β' are constants and the second term is due to the deactivation of the catalyst by dimerization.[2] However, in the region where the catalyst concentration was higher than 1.0×10^{-3} *M*, the initial rate of the transfer hydrogenation had first-order dependence on the catalyst concentration and was expressed in the form: R =