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Effects of Molecular Nitrogen on Coordination-Metal Catalysis

I. Inhibiting Influence of Dinitrogen on the Isomerization of 1-Pentene Catalyzed by Dihydrido(dinitrogen)tris(triphenylphosphine)ruthenium*

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The isomerization of 1-pentene is catalyzed by $RuH_2(N_2)(PPh_3)$, in toluene at 25°C. The reaction shows two distinct stages: it proceeds very rapidly initially and is accompanied by formation of 1 mole of pentane per mole of catalyst; then the rate quickly declines and the reaction follows first order kinetics. In both stages the isomerization is retarded by the addition of N_2.

The kinetic data suggest that the catalytically active species are $RuH_2(PPh_3)_3$ in the first stage of the isomerization and $Ru(PPh_3)_3$ in the second stage. The inhibiting effects of N_2 are attributed to the ability of N_2 to compete with the olefin for coordination to the metal. Infrared and NMR spectroscopic data lend support to this conclusion.

INTRODUCTION

Molecular nitrogen is often used to provide an inert atmosphere for reactions of alkenes catalyzed by homogeneous transition metal systems. The discovery of stable dinitrogen–transition metal complexes, in particular of those in which N_2 can be reversibly exchanged with ethylene (*1*), suggested that in fact dinitrogen may influence the course of these catalyzed reactions. But no evidence of this has been reported, even in catalysts which contain coordinated N_2. For example, Kovacs, Speier and Marko (*2*) studied the effects of N_2 on the isomerization of hexene catalyzed by $Co(N_2)(PPh_3)_3$ and observed no inhibition of the reaction by N_2.

Because of their considerable practical importance, we have undertaken a systematic study of the effects of N_2 on homogeneous coordination catalysis of olefins. We report here a study of the isomerization of 1-pentene catalyzed by $RuH_2(N_2)(PPh_3)_3$ and of the influence of N_2 on the isomerization rate. The results of this study clearly indicate that molecular nitrogen has a strong inhibiting influence on this reaction.

EXPERIMENTAL METHODS

All manipulations were carried out in an atmosphere of argon unless indicated otherwise. Infrared spectra were measured on a Perkin-Elmer 257 grating infrared spectrophotometer. NMR spectra were measured on a Varian T-60 NMR spectrometer.

Catalysts. $RuH_4(PPh_3)_3$ and $RuH_2(N_2)(PPh_3)_3$ have been described by Knoth (*3*) who prepared them by the reaction of $RuHCl(PPh_3)_3$ with Et_3Al under argon and under dinitrogen, respectively. We prepared the tetrahydride by the reaction of $RuCl(PPh_3)_3$ with $NaBH_4$ in methanol according to the following procedure.

Dichloro-tris (triphenylphosphine) ruthenium (1.0 g, 1.04 mmole) was dispersed in 25 ml methanol. A pellet of sodium tetrahydroborate (0.25 g, 6.6 mmole) was added to the solution with rapid stirring under a slow stream of hydrogen. After 30 min the mixture was filtered and the precipitate was washed with methanol. The precipitate was

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again placed in 25 ml methanol and another pellet of $NaBH_4$ was added to the dispersion. The product was collected by filtration, washed with MeOH and dried in vacuum. The yield was 0.84 g (91%). *Anal.* calculated for $C_{54}H_{49}P_2Ru$: C, 72.7; H, 5.54; P, 10.9. Found: C, 72.6; H, 5.62; P, 10.5; Cl, <0.01.

The dinitrogen complex was obtained by the reaction of N_2 with $RuH_4(PPh_3)_3$ in cyclohexane. $RuH_2(N_2)(PPh_3)_3$ is characterized by a sharp band at 2146 cm^{-1}, which is the strongest band in the infrared spectrum.

Isomerization tests. Solutions of the catalysts (0.2–2.0 m*M*) were prepared by dissolving a known weight of the complex in toluene. Twenty milliliters of solution were placed in a Diehls-Alder tube which was sealed with a neoprene septum. The tube was transferred to a water bath at 25°C, and the solution was stirred with a magnetic stirrer for about 15 min, before a known volume of oxygen-free pentene was added with a syringe. Liquid samples (10 μl) were removed at regular intervals and analyzed by vpc using a 6.7 *m* bis[2-(2-methoxyethoxy)ethyl] ether column.

Catalyst solutions which were not used immediately after their preparation were kept at dry ice-acetone temperature (−76°C).

For the experiments carried out under dinitrogen the catalyst solution was swept with N_2 for 1 hr, before adding the olefin. To flush out the N_2 after addition of the pentene, the solution was cooled to dry ice-acetone temperature and swept with argon for 1 hr or more.

Reactants. Pentene-1 (Phillips Research grade), pentene-2 (Phillips Pure grade) and toluene were dried over magnesium oxide in argon before use. The 2-pentene contained 25% of the *cis* and 75% of the *trans* isomers.

RESULTS

A. Isomerization of 1-Pentene

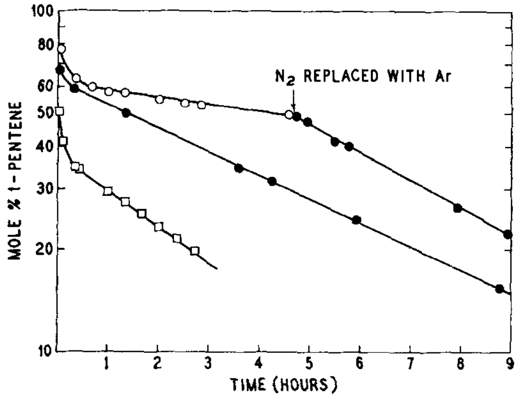

FIG. 1. Isomerization of 1-pentene (1.8 *M*) in toluene at 25°C catalyzed by 2.2×10^{-3} *M*: (□) $RuH_4(PPh_3)_3$ under 1 atm Ar; (●) $RuH_2(N_2)(PPh_3)_3$ under 1 atm Ar; (○) $RuH_2(N_2)(PPh_3)_3$ under 2 atm N_2; $[N_2] = 1.4 \times 10^{-2}$ *M*.

Fresh solutions $RuH_2(N_2)(PPh_3)_3$ (I) in toluene catalyzed the isomerization of 1-pentene rapidly at 25°C. Typical results obtained under argon and under N_2 are presented in Fig. 1. Also shown in this figure are the results obtained in a nitrogen-free system using $RuH_4(PPh_3)_3$ (II) as the catalyst. In all three experiments the reaction exhibited two distinct stages: it proceeded very rapidly initially, then quickly declined and followed first order kinetics. The reaction rate both initially and in the second stage was lower with I than with II; it was reduced further under N_2. The inhibiting effects of N_2 were reversed when the dissolved N_2 was removed by sweeping the solution with argon. The measured rate constants, k_{obs}, in the second stage of the reaction (see below) were for:

$RuH_4(PPh_3)_3$	under Ar	4.4×10^{-3} min^{-1}
$RuH_2(N_2)(PPh_3)_3$	under Ar	2.7×10^{-3} min^{-1}
$RuH_2(N_2)(PPh_3)_3$	under N_2	8.5×10^{-4} min^{-1}

Preferential formation of *trans*-2-pentene, in excess of the *trans/cis* equilibrium value, occurred with both catalysts. This is illustrated in Fig. 2, where the *trans:cis* ratio is plotted against time.

During the initial stage isomerization was accompanied by hydrogenation: 1 mole of pentane was formed/mole of I and 2 moles of pentane/mole of II. This corresponds to the consumption of all the hydridic hydrogen in I and II. The rate of isomerization with I was at least 250 times

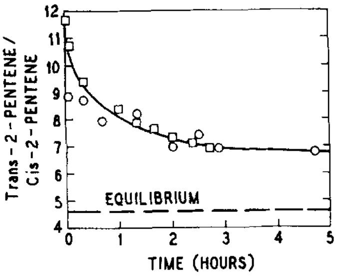

FIG. 2. *Trans/cis* isomer ratio in the product of the isomerization of 1-pentene (1.8 *M*) catalyzed at 25°C by $2.2 \times 10^{-3} M$: (□) $RuH_4(PPh_3)_3$ under Ar; (○) $RuH_2(N_2)(PPh_3)_3$ under 2 atm N_2.

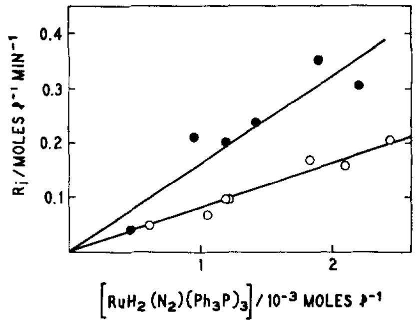

FIG. 3. Variation of initial rates of isomerization (R_i) of 1-pentene at 25°C with $[RuH_2(N_2)(PPh_3)_3]$ at 25°C; [pentene] = 1.2 *M*: (○) under 1 atm N_2; (●) under 1 atm Ar.

faster than the rate of hydrogenation. Little or no pentane was formed during the second stage of the reaction, but after 1 day or more as much as an additional 1 mole of pentane was produced. This suggests that hydrogen was slowly abstracted from the phenyl groups of the triphenylphosphine (*7*). The catalyst then became inactive, but the activity could be restored by passing H_2 through the solution.

Removal of all of the hydride ligands from I and II by formation of pentane is a selective process which occurs rapidly only with the terminal olefin. When 2-pentene was added to the catalyst solution only 1 mole of pentane was formed/mole of II and no pentane was formed with I. After several hours an additional 1 mole of pentane/mole of catalyst was formed gradually, perhaps by hydrogenation of the 1-pentene produced by isomerization (equilibrium concentration of 1-pentene at 25°C ca. 2%). As a consequence of this selectivity, results such as those shown in Fig. 1 are obtained only with 1-pentene concentrations at least 250 times as large as the catalyst concentration. At lower olefin to catalyst ratios, near-equilibrium concentrations of 2-pentene are reached before consumption of all the hydridic hydrogen is complete, and the two stages of the reaction cannot be readily differentiated.

The dependence of the initial rates of 1-pentene isomerization on the concentration of I is shown in Fig. 3. These rates were obtained from the 1-pentene conversions at 1 min. They are of limited value since, as indicated by the formation of pentane, the initial catalytic species was rapidly consumed. However, they show that molecular nitrogen retards the initial isomerization reaction over the entire range of catalyst concentration used.

In the second stage of the reaction there is no evidence of significant changes in the catalytically active species. The reaction rates are slower and are more amenable to standard kinetic treatment. The measured rate constants, k_{obs}, were obtained as the slope of the plot for a first order reversible reaction (*4*). As shown in Fig. 4, these rate constants increased nonlinearly with catalyst concentration and were lower in the presence of N_2. In Fig. 4 the experiments

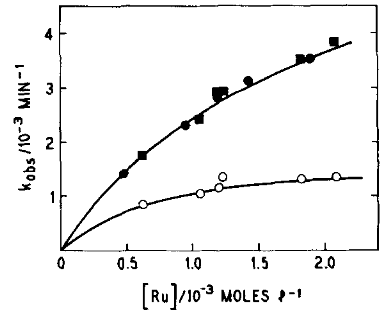

FIG. 4. Second stage of the isomerization of 1-pentene catalyzed by $RuH_2(N_2)(PPh_3)_3$: the measured rate constant, k_{obs}, at 25°C as a function of the catalyst concentration; [pentenes] = 1.2 *M*: (●) under 1 atm Ar; (○) under 1 atm N_2; (■) under 1 atm Ar after removal of N_2 (see text).

represented by the full circles were carried out entirely under argon. Those represented by open circles were first carried out under N_2. The dinitrogen was then removed as described in the experimental section and the measurements continued under argon (full squares).

B. Effects of O_2

Because the catalytic properties of I and II are readily destroyed by exposure to air of either the solid complexes or of their solutions, the effects of O_2 on the isomerization of 1-pentene catalyzed by I were also studied and were compared to those produced by N_2. The results, which are summarized in Table 1, show that dioxygen is a permanent inhibitor (i.e., its effects on the isomerization reaction persisted after the solution was swept with argon to remove any dissolved O_2) while dinitrogen is a temporary inhibitor. Thus, the retardation of the isomerization of 1-pentene by N_2 cannot be attributed to accidental contamination of the solutions with air. In fact, such contamination is readily detected. Fresh solutions of I or II in toluene were pale yellow or pale pink; when saturated with N_2 they become paler, while on addition of O_2 they darkened.

C. Isomerization of 2-Pentene

In toluene solution a mixture of 25% *cis*, 75% *trans*-2-pentene was isomerized by I under Ar to equilibrium concentration of 1-pentene without significant formation of pentane. The isomerization proceeded more rapidly when catalyzed by II and was accompanied by the formation of 1 mole of pentane/mole of II. Added N_2 inhibited the isomerization process severely; the initial rate of isomerization with I was 18 times faster under argon than under dinitrogen. The formation of 1-pentene with time for these experiments is shown in Fig. 5.

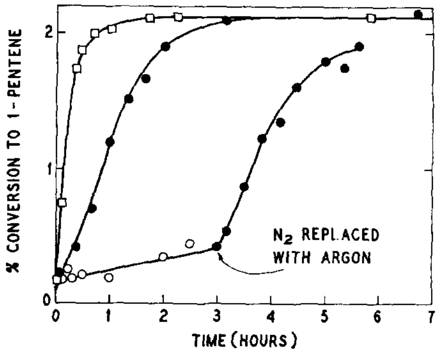

FIG. 5. Isomerization of 2-pentene (1.8 *M*) in toluene at 25°C catalyzed by 2.2×10^{-3} *M*: (□) $RuH_4(PPh_3)_3$ under 1 atm Ar; (●) $RuH_2(N_2)(PPh_3)_3$ under 1 atm Ar; (○) $RuH_2(N_2)(PPh_3)_3$ under 2 atm N_2.

D. Infrared and NMR data

$RuH_2(N_2)(PPh_3)_3$ and $RuH_4(PPh_3)_3$. The infrared spectrum of I is characterized by a strong band at 2146 cm^{-1}, which is broader in solution than in the solid (Nujol mull). The high-field ^1H NMR spectrum of I in deuterobenzene under N_2 at 30°C contained a complex pattern of broad overlapping peaks from 7 to 11 ppm above TMS and a single broad peak at 12.8 ppm above TMS. The limited solubility of the complex precluded intensity measurements.

The high-field ^1H NMR spectrum of II

TABLE 1

THE INFLUENCE OF O_2 AND N_2 ON THE ISOMERIZATION OF 1-PENTENE CATALYZED BY $RuH_2(N_2)(PPh_3)_3$[a]

Atmosphere	Moles O_2/ mole catalyst	Initial rate (moles/liter/min)	$k_{obs}/10^{-3}$ min^{-1} for the second stage: Before Ar flush	$k_{obs}/10^{-3}$ min^{-1} for the second stage: After Ar flush
Argon	0	0.20	2.8	—
Argon + oxygen	0.5	0.033	0.84	0.83
Argon + oxygen	0.25	0.066	1.4	1.4
Nitrogen	0	0.095	1.14	2.9

[a] [Pentene] = 1.2 *M*; $[RuH_2(N_2)(PPh_3)_3]$ = 1.2×10^{-3} *M*; 25°C, 1 atm.

in deuterobenzene showed only a broad featureless resonance at 7 ppm above TMS. Intensity measurements in solutions of II saturated with H_2 at 1 atm indicated only 2 to 2.3 protons/Ru. Knoth (*3*) also has obtained low values (3 to 3.2 H/Ru) for the intensity of the hydride resonance of the tri-*p*-tolyl-phosphine analog of II.

When hydrogen was removed by sweeping the solution of II with argon, the intensity of the band at 7 ppm above TMS decreased, but no new signal was observed. Removal of N_2 from a solution of I saturated with N_2, caused loss of coordinated N_2, demonstrated by a reduction in the intensity of the band at 2146 cm^{-1}. In the ^1H NMR spectrum the intensity of the high-field resonances of I also decreased, and a band similar to that observed in the spectrum of II was formed at 7 ppm above TMS.

Reaction of $RuH_4(PPh_3)_3$ with 2-pentene. When an excess of 2-pentene was added to a deuterobenzene solution of II, the resonance at 7 ppm above TMS disappeared within a few minutes and a broad quartet was formed centered at 10 ppm above TMS (J = 37 Hz).

The reaction in the absence of a solvent of II with 2-pentene (1 hr at ambient temperature) yielded a yellow solid which was recovered by removal of the pentene under a stream of argon followed by drying in vacuum for 3 hr. The reaction was accompanied by formation of 1.1 moles of pentane/mole of II. A deuterobenzene solution of this solid showed the ^1H NMR spectrum of pentene downfield from TMS and the quartet at 10 ppm above TMS. The solid was not sufficiently soluble for intensity measurements. On addition of N_2 to the deuterobenzene solution, I, identified by both its infrared and ^1H NMR spectrum, was formed. The reaction of the solid with $CDCl_3$ yielded $RuHCl(PPh_3)_3$ identified by its ^1H NMR spectrum (*5*).

Reaction of $RuH_2(N_2)(PPh_3)_3$ with 2-pentene. Addition of a 10-fold excess of 2-pentene to a deuterobenzene solution of I saturated with N_2 at 1 atm, had no pronounced effect on the infrared and ^1H NMR spectra of I. The band at 2146 cm^{-1} showed no significant decrease in intensity and remained essentially unchanged after 4 hr. When the solution was swept with argon to remove the dissolved N_2, this band rapidly diminished in intensity and finally disappeared altogether. In the high-field ^1H NMR spectrum the peaks assigned to the hydride hydrogen of I also disappeared and a broad quartet appeared at 10 ppm above TMS (J = 37 Hz). On readmission of N_2 (10 min sweep of the solution), I was regenerated, as indicated by the reappearance of both its high-field NMR spectrum and of a strong band at 2146 cm^{-1} in the infrared spectrum.

Reaction of $RuH_2(N_2)(PPh_3)_3$ with 1-pentene. As indicated by the rate of pentane formation in the isomerization studies, the formation of a zerovalent complex from the reaction of I with pentenes occurs rapidly only with 1-pentene. Yet, even with the α-olefin, stoichiometric amounts of pentane are obtained readily only when the initial concentration of 1-pentene is several hundred times greater than that of I; otherwise, equilibrium distribution of the pentene isomers is achieved before the hydrogenation reaction is complete. Accordingly, when 15 moles of 1-pentene/mole of I were added to a deuterobenzene solution of I under 1 atm of N_2, 90% of the 1-pentene was converted to 2-pentene and 0.18 mole of pentane was formed/mole of I during the first minute; during the following 24 hr only 0.15 additional mole of pentane/mole of I was formed.

Repeatedly, the concentration of the pentenes was reduced under a stream of argon, and 1-pentene was added, until no more pentane was formed. At this point no peaks were observed in the high-field region of the NMR spectrum. Exposure of the solution to N_2 caused no change in the NMR spectrum; in the ir spectrum no absorption was observed at 2146 cm^{-1} but a new strong band was formed at 2115 cm^{-1}. Treatment of the solution with H_2, then with N_2, regenerated I.

DISCUSSION

The broadening of the band at 2146 cm^{-1} in the solution infrared spectrum of I and the broad features of the hydride resonances in the ^{1}H NMR spectrum of I and II indicate that ligand dissociation takes place in solution for both complexes. The loss of coordinated N_2 from I when N_2 was removed from solutions of I and the decrease in the intensity of the hydride resonance in the NMR spectrum of II when H_2 was removed from solutions of II are consistent with the dissociation in solution of N_2 from I and of H_2 from II,

$$\underset{\mathrm{I}}{\mathrm{RuH_2(N_2)(PPh_3)_3}} \rightleftarrows \mathrm{RuH_2(PPh_3)_3} + \mathrm{N_2}, \quad (1)$$

$$\underset{\mathrm{II}}{\mathrm{RuH_4(PPh_3)_3}} \rightleftarrows \mathrm{RuH_2(PPh_3)_3} + \mathrm{H_2}. \quad (2)$$

Accordingly, donor molecules such as NH_3, CO, R–CN and PPh_3 react with I and II to give by replacement of N_2 and H_2, respectively, dihydride complexes analogous to I (*3*, *6*).

The reaction of I with pentenes also yields a dihydride complex (III) by replacement of the N_2 by the olefin,

$$\underset{\mathrm{I}}{\mathrm{RuH_2(N_2)(PPh_3)}} + \mathrm{C_5H_{10}} \rightleftarrows \underset{\mathrm{III}}{\mathrm{RuH_2(C_5H_{10})(PPh_3)_3}} + \mathrm{N_2}, \quad (3)$$

then hydrogenation of the olefin takes place yielding the zerovalent-complex IV,

$$\underset{\mathrm{III}}{\mathrm{RuH_2(C_5H_{10})(PPh_3)_3}} \xrightarrow{\mathrm{C\ H}} \underset{\mathrm{IV}}{\mathrm{Ru(C_5H_{10})(PPh_3)_3}} + \mathrm{C_5H_{12}}. \quad (4)$$

Evidence that the latter process occurs is given by the formation of 1 mole of pentane/mole of I and by the disappearance of the hydride resonances in the ^{1}H NMR spectrum.

Ethylene and styrene have been shown (*7*) to give analogous zerovalent complexes $Ru(C_2H_4)(PPh_3)_3$ and $Ru(CH_2{=}CHC_5H_6)(PPh_3)_3$.

Because, as with other ruthenium species (*5*), the hydrogenation reaction occurs readily only with terminal olefins, III is obtained as a stable intermediate from the reaction of 2-pentene with I. The inhibition of this reaction by N_2, the disappearance of the band at 2146 cm^{-1} when N_2 is removed from the solution, and the fact that the same species is obtained from the reaction of 2-pentene with II show that N_2 is in fact the ligand replaced by the olefin. III is characterized as a hydride by its NMR spectrum which contains a quartet in the hydride region, by its reaction with $CDCl_3$ which yields $RuHCl(PPh_3)_3$, and by its reaction with N_2 which yields I. The presence of a quartet in the hydride region of the NMR spectrum also suggests that in solution the hydride ligands couple with three equivalent phosphorus nuclei.

In view of these observations it seems reasonable that the isomerization of 1-pentene catalyzed by I proceeds by formation [Eq. (3)] of IIIa which is then followed both by isomerization,

$$\underset{\mathrm{IIIa}}{\mathrm{RuH_2(1\text{-}C_5H_{10})(PPh_3)_3}} \rightleftarrows \underset{\mathrm{IIIb}}{\mathrm{RuH_2(2\text{-}C_5H_{10})(PPh_3)_3}}, \quad (5)$$

and by hydrogenation [Eq. (4)].

The inhibition of the isomerization by added N_2 (Fig. 3) is consistent with the path described by Eqs. (1) and (3). Because the catalytic species active in the initial stage of the isomerization is rapidly depleted by the irreversible formation of pentane, the initial isomerization rates are of limited value for the clarification of the reaction mechanism. The similarity in the general course of the isomerization reaction carried out under N_2 and of that carried out in the nitrogen free system using II as the catalyst (Fig. 1), including the preferential formation of *trans*-2-pentene (Fig. 2), indicates that N_2 does not affect the mechanism of the reaction. It only influences the reaction rate as a consequence of the greater stability of I than of III. Clearer evidence of such difference in stability is provided for 2-pentene by the spectroscopic data (*8*) and by the reversible inhibiting effects of added N_2 on the isomerization rate (Fig. 5).

The pentane formed during the initial stage of the isomerization of 1-pentene corresponds to the consumption of all the hydride ligands of I. So the catalytic species in the second stage of the reaction can be formulated as the zero-valent complex IV. Probably the catalytic process now involves participation of *ortho* hydrogens of the triphenyl phosphine ligands; evidence has been reported (7) for the exchange of *ortho* hydrogens with ethylene hydrogens in the ethylene analogue of IV.

The positive fractional order in I and the inhibition of the isomerization by added N_2 (Fig. 4) show that in the second stage the catalytically active species is formed by dissociation of N_2 from a nitrogen-coordinated complex. The occurrence of this complex is demonstrated by the formation, in the presence of N_2, of the band at 2115 cm^{-1} in the infrared spectrum of the solution, which we attribute to $\nu_{N\equiv N}$ of $RuN_2(PPh_3)_3$. So, if no additional ligand dissociation takes place, the active catalyst concentration in the presence of N_2 is regulated by the equilibrium

$$\underset{V}{Ru(N_2)(PPh_3)_3} + C_5H_{10} \rightleftarrows \underset{IV}{Ru(C_5H_{10})(PPh_3)_3} + N_2, \quad (6)$$

while in a nitrogen-free system the concentration of IV is equal to the initial concentration of II. The equilibrium constant for the process described in Eq. (6) was calculated from the data reported in Fig. 1, assuming that the measured rate constants for the isomerization of 1-pentene catalyzed by II under argon and by I under N_2 are directly proportional to the concentration of IV. The value of the equilibrium constant was found to be 2×10^{-3}. Using this value, the concentration of IV was calculated for the experiments summarized in Fig. 4. As shown in Fig. 6 a linear dependence of the measured rate constants, k_{obs}, on the concentration of IV was obtained. It seems therefore that the inhibition by N_2 of the isomerization of 1-pentene in the second stage is also a consequence of the greater affinity of N_2 than of the pentene for the catalytically active species.

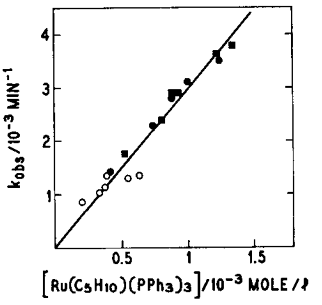

FIG. 6. Second stage of the isomerization of 1-pentene catalyzed by $RuH_2(N_2)(PPh_3)_3$: the measured rate constant, k_{obs}, at 25°C as a function of $Ru(C_5H_{10})(PPh_3)_3$ calculated as described in the text. (●) Under 1 atm Ar; (○) under 1 atm N_2; (■) under 1 atm Ar after removal of N_2 (see text).

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