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EFFECTS OF MOLECULAR NITROGEN ON THE REACTIVITY OF COORDINATION COMPOUNDS: ACCELERATION AND INHIBITION BY N_2 OF THE ISOMERIZATION OF 1-PENTENE CATALYZED BY COBALT AND RUTHENIUM COMPLEXES

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SUMMARY

The double bond migration in *n*-pentenes is inhibited by N_2 in the presence of ruthenium catalysts whose precursor is $RuH_4(PPh_3)_3$, and is promoted by N_2 in the presence of a cobalt catalyst whose precursor is $CoH_3(PPh_3)_3$.

Spectroscopic and kinetic data indicate that the active ruthenium species are $RuH_2(PPh_3)_3$ and $Ru(PPh_3)_3$; the inhibition by N_2 is attributed to the ability of N_2 to compete with the olefin for coordination to the ruthenium. For the process, $Ru(N_2)(PPh_3)_3 + C_5H_{10} \rightleftharpoons Ru(C_5H_{10})(PPh_3)_3 + N_2$, the equilibrium constant, calculated from kinetic data, is 2×10^{-3} at 25°C.

In the isomerization catalyzed by $CoH_3(PPh_3)_3$ the rate determining step is the displacement of the product olefin by the reactant olefin. It is proposed that the observed promotion of the isomerization rate by N_2 is due to the catalytic effects of N_2 on the olefin exchange reaction.

INTRODUCTION

The influence of molecular nitrogen on reactions of olefins catalyzed by coordination compounds is of considerable interest, particularly in view of the widespread practice of carrying out these reactions under N_2. This practice is founded on the assumption that N_2 provides an inert atmosphere and does not influence the course of the catalyzed reaction. The purpose of this paper is to show that dinitrogen may in fact affect the stability and reactivity of coordination compounds which are intermediates in coordination-catalyzed reactions of olefins, and that it may influence the course of the catalyzed reactions. We shall discuss the migration of the double bond in normal pentenes catalyzed by cobalt and ruthenium species, whose precursors are $CoH_3(PPh_3)_3$ and $RuH_4(PPh_3)_3$ or their dinitrogen analogues $CoH(N_2)(PPh_3)_3$ and $RuH_2(N_2)(PPh_3)_3$, and the effects of N_2 on these reactions. The results of this study show that dinitrogen may react with catalytically active intermediates and form compounds that are stable toward substitution of N_2 by olefins, or that N_2 may otherwise modify the reactivity of an intermediate so that the catalzyed reaction is either inhibited or promoted, and the product distribution is altered, in the presence of N_2.

RUTHENIUM COMPLEXES

The reaction of pentenes with $RuH_4(PPh_3)_3$, (i), or with $RuH_2(N_2)(PPh_3)_3$, (ii), yields the pentene-coordinated complex (iii):

$$\underset{\text{(i)}}{RuH_4(PPh_3)_3} + 2C_5H_{10} \rightarrow RuH_2(C_5H_{10})(PPh_3)_3 + C_5H_{12} \qquad (1)$$

$$\underset{\text{(ii)}}{RuH_2(N_2)(PPh_3)_3} + C_5H_{10} \rightleftharpoons \underset{\text{(iii)}}{RuH_2(C_5H_{10})(PPh_3)_3} + N_2 \qquad (2)$$

Then hydrogenation of the olefin takes place with formation of the zerovalent complex (iv):

$$RuH_2(C_5H_{10})(PPh_3)_3 \xrightarrow{C_5H_{10}} \underset{\text{(iv)}}{Ru(C_5H_{10})(PPh_3)_3} + C_5H_{12} \qquad (3)$$

The latter reaction occurs rapidly only with the terminal olefin. Evidence for the processes described in eqns. (1)—(3) is provided by the spectroscopic observations and kinetic data discussed below. These data also show that the equilibrium in eqn. (2) lies to the left.

IR and NMR data

The high-field ^1H NMR spectrum of (i) in C_6D_6 at 30°C contains only a broad featureless resonance at 7 p.p.m. above TMS [1, 2]. On addition of an excess of 2-pentene (25% *cis*, 75% *trans*) to a C_6D_6 solution of (i) this signal disappeared within a few minutes and a quartet was formed centered at 10 p.p.m. above TMS ($J = 37$ Hz), suggesting that a fluxional tris(triphenylphosphine)hydride was formed. The reaction of 2-pentene with (i), which was accompanied by the formation of 1.1 mole of pentane/mole of (i) produced a yellow solid, whose ^1H NMR spectrum in C_6D_6 contained peaks assignable to pentene downfield from TMS and the quartet at 10 p.p.m. above TMS. The limited solubility of the solid precluded intensity measurements. On exposure of a C_6D_6 solution of this compound to N_2, (ii) was formed. The solid also yielded $RuHCl(PPh_3)_3$ by reaction with $CDCl_3$. These data are consistent with the formation of the pentene-coordinated complex, (iii), according to eqn. (1), and with the assignment of the quartet at 10 p.p.m. above TMS to the two hydridic hydrogens of (iii).

When an excess of 2-pentene was added to a C_6D_6 solution of (ii) under 1 atm. of N_2, no significant changes were observed in the high-field ^1H NMR spectrum [1] of (ii) or in the intensity of the band at 2146 cm^{-1} ($\nu_{N\equiv N}$) in the IR spectrum, even after several hours. However, when N_2 was removed by sweeping the solution with argon, (iii), identified by its high-field ^1H NMR spectrum, was formed. On readmission of N_2, (ii) was rapidly regenerated. Both the inhibition by N_2 of the forward reaction described by eqn. (2) and the rapid formation of (ii) from (iii) in the presence of an excess of the olefin (pentene:N_2 ca. 10:1) establish that (ii) is much more stable than the 2-pentene-coordinated complex (iii).

The relative stabilities of (ii) and of the 1-pentene-coordinated complex, (iii), could not be determined by this method, but rate data (see below) indicate that (ii) is more stable.

When a solution of (i) was treated with a large excess of 1-pentene, two moles of pentane were formed per mole of (i), and no signal was observed in the hydride region, in accord with the processes described by eqns. (1) and (3). After exposing the solution to N_2 a strong band developed at 2115 cm^{-1} in the IR spectrum, which we attribute to ν_{N-N} of $Ru(N_2)(PPh_3)_3$, (v). Since (v) was formed in the presence of an excess of the pentene, it also is more stable than (iv).

Isomerization studies

Solutions of (i) or (ii) in toluene catalyzed the isomerization of 1-pentene rapidly at 25°C. Typical results obtained with (i) under Ar and with (ii) under Ar and under N_2 are presented in Fig. 1. The reaction exhibited two 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 (ii) than with (i); it was further reduced under N_2, but the inhibiting effects of N_2 were removed by sweeping the solution with argon. Preferential formation of *trans*-2-pentene, in excess of the *trans/cis* equilibrium value, occurred with both catalysts [3].

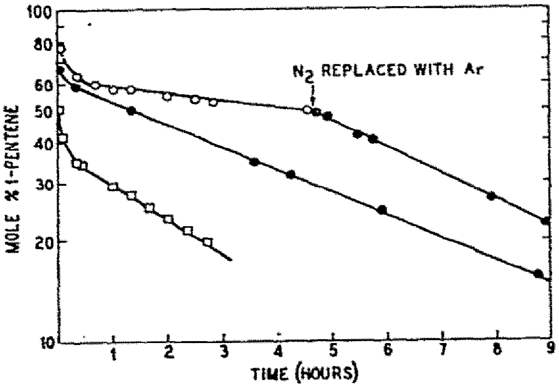


Fig. 1. Isomerization of 1-pentene (1.8 *M*) in toluene at 25°C catalyzed by 2.2 × 10^{-3} *M*: (□) $RuH_4(PPh_3)_3$ under 1 atm. Ar; (●) $RuH_2(N_2)(PPh_3)_3$ under 1 atm. Ar; (○) $RuH_2(N_2)(PPh_3)_3$ under 2 atm. N_2; $[N_2]$ = 1.4 × 10^{-2} *M*.

During the initial stage, isomerization was accompanied by hydrogenation: one mole of pentane was formed per mole of (ii) and two moles of pentane per mole of (i). The rate of isomerization was at least 250 times faster than the rate of hydrogenation.

These results can be readily interpreted on the basis of the spectroscopic observations discussed above. The isomerization of 1-pentene catalyzed by (i) or (ii) proceeds by formation (eqn. (1) or (2)) of (iiia), which is then followed concurrently by isomerization

$$\underset{\text{(iiia)}}{RuH_2(1\text{-}C_5H_{10})(PPh_3)_3} \rightleftharpoons \underset{\text{(iiib)}}{RuH_2(2\text{-}C_5H_{10})(PPh_3)_3} \qquad (4)$$

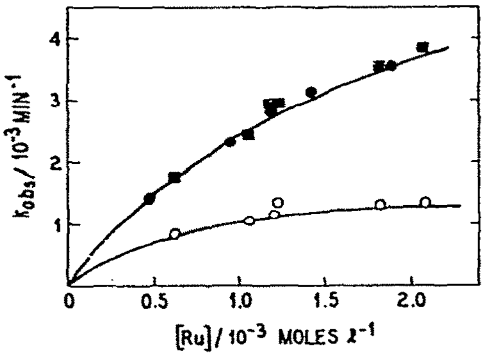
and by hydrogenation (eqn. (3)).

The catalytic species in the second stage of the reaction can be formulated as the zerovalent complex (iv). Probably the catalytic process now involves participation of *ortho* hydrogens of the triphenylphosphine ligands.

In the isomerization of 2-pentene to 1-pentene no pentane was formed from (ii) and only one mole of pentane was formed per mole of (i), so that the catalytic active species was (iii) throughout. In experiments carried out under the same conditions and at the same concentrations as in Fig. 1, using 2-pentene (25% *cis*, 75% *trans*) as the starting olefin, the initial rates of isomerization to 1-pentene catalyzed by (ii) was 18 times faster under argon than under N_2 [3, 4]. Similarly severe inhibition by N_2 was observed when the reaction was carried out without solvent. The hydrogenation of 2-pentene was also inhibited by N_2 [4]. These results confirm that N_2 has much greater affinity than 2-pentene for the $RuH_2(PPh_3)_3$ moiety, as already indicated by the spectroscopic evidence discussed previously.

The data shown in Fig. 1 show that the initial rate of isomerization of 1-pentene is also retarded by N_2. Initial rates, obtained from conversion at 1 min, at several concentrations of (ii) (from 0.5 to 2.5×10^{-3} *M*) indicate that the reaction occurs twice as rapidly under 1 atm. of Ar than under 1 atm. of N_2 [3]. Although these initial rates are of limited value, because the initial catalytic species is rapidly consumed, they indicate that (ii) is also more stable than (iiia). Moreover they also suggest that (iiia) is more stable than (iiib).

In the second stage of the isomerization of 1-pentene there is no evidence of significant changes in the catalytically active species. The reaction rates are much slower than in the first stage and are more amenable to standard kinetic treatment. The dependance of the measured rate constants, k_{obs}, (obtained as the slope of the plot for a first order reversible reaction) on the concentration of (ii) is shown in Fig. 2. The experiments represented by full circles were carried entirely under Ar. Those represented by open circles were first performed under N_2; the N_2 was then swept out with argon at −76°C, and the measurements continued under Ar (full squares). The positive fractional order in (ii) and the inhibiting effects of N_2 are consistent with the formation of the catalytically active species by dissociation of N_2. So, if no additional



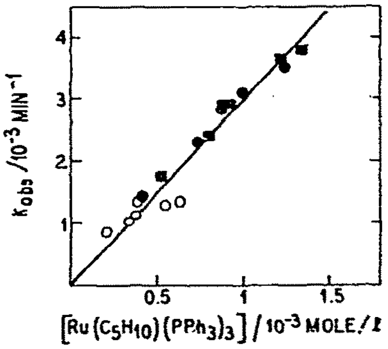


Fig. 2. Second stage of the isomerization of 1-pentene catalyzed by $RuH_2(N_2)(PPh_3)_3$. The measured rate constant, k_{obs}, at 25°C as a function of the catalyst concentration, [pentenes] = 1.2 *M*. (●) under 1 atm. Ar; (○) under 1 atm. N_2; (■) under 1 atm. Ar after removal of N_2.

Fig. 3. 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 $[Ru(C_5H_{10})(PPh_3)_3]$: (●) under 1 atm. Ar; (○) under 1 atm. N_2; (□) under 1 atm. Ar after removal of N_2.

dissociation takes place, the active catalyst concentration in the presence of N_2 is regulated by the equilibrium,

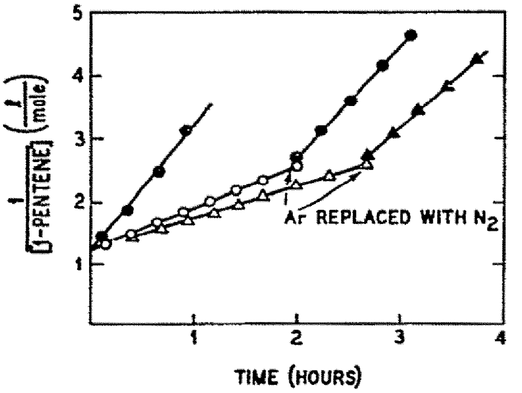
$$\underset{(v)}{Ru(N_2)(PPh_3)_3} + C_5H_{10} \rightleftharpoons \underset{(iv)}{Ru(C_5H_{10})(PPh_3)_3} + N_2 \qquad (5)$$

while in a nitrogen-free system the concentration of (iv) is equal to the initial concentration of (i). The equilibrium constant for the process described in eqn. (5), calculated from the data reported in Fig. 1, was found to be 2×10^{-3}. Using this value, the concentration of (iv) was calculated for the experiments summarized in Fig. 2. As shown in Fig. 3, a linear dependence of the measured rate constants, k_{obs}, on the concentration of (iv) was obtained.

COBALT COMPLEXES

The activity for double bond migration of $CoH(N_2)(PPh_3)_3$ was first reported by Yamamoto et al. [5], who did not consider the effect of added N_2 on the reaction. Tyrlik [6] discussed the mechanism of the isomerization of *cis*-2-pentene to *trans*-2-pentene catalyzed by $CoH(N_2)(PPh_3)_3 \cdot Et_2O$, (vi), but did not elucidate the effects of added N_2 on the reaction. Kovacs et al. [7] studied the isomerization of the 1-hexene catalyzed by $Co(N_2)(PPh_3)_3$, and found no inhibition of the reaction by added N_2. We have studied the isomerization of 1-pentene to 2-pentene and that of *cis*-2-pentene to *trans*-2-pentene catalyzed by (vi) and by $CoH_3(PPh_3)_3$, (vii), and have found that added N_2 promotes these reactions.

The isomerization of 1-pentene to 2-pentene catalyzed by (vi) in toluene,



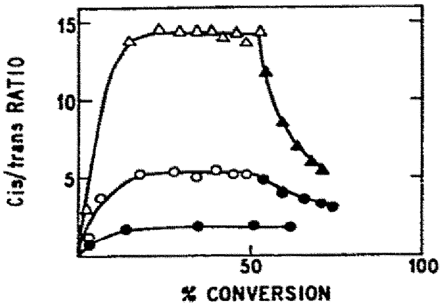


Fig. 4. Second-order plot for the isomerization of pentene in toluene at 25°C and atmospheric pressure catalyzed by $CoH(N_2)(PPh_3)_3 \cdot Et_2O$: (○) under Ar; (●) under N_2 $CoH_3(PPh_3)_3$; (△) under Ar; (▲) under N_2; [pentene] = 0.83 mole/l [Co] = 2.4×10^{-3} mole/l.

Fig. 5. *Cis/trans* isomer ratio in the products of the isomerization of 1-pentene.

or in the absence of solvent, at 25° C yielded preferentially *cis*-2-pentene. The reaction was second order in 1-pentene, and first order in (vi) (0.0024 to 0.014 *M*), was promoted by the addition of N_2, and was retarded by the addition of triphenyl phosphine. The effects produced by N_2 are illustrated in Fig. 4 where the isomerization is plotted on a second order reaction for experiments performed under argon and under dinitrogen. Also shown in the figure are the results obtained in a nitrogen-free system, using (vii) as the catalyst, and the effects produced on this system by addition of N_2.

In addition to promoting the isomerization of 1-pentene, dinitrogen also affected the isomer distribution in the product, as shown in Fig. 5, where the *cis/trans* ratio is plotted as a function of conversion for the experiments shown in Fig. 4.

The isomerization of *cis*-2-pentene to *trans*-2-pentene catalyzed by (vi) was also enhanced by N_2. Tyrlik [6] has reported that this reaction, which he studied only under N_2, occurs without formation of 1-pentene. We observed formation of 1-pentene both under argon and under dinitrogen.

At the catalyst concentrations used (0.5 to 2.5×10^{-2} *M*) approximately 1.5 moles of pentane per mole of (vii) and 0.5—0.7 moles of pentane per mole of (vi) were formed when the olefin was added. The hydrogenation reaction occurred either under argon or under N_2 and was complete within 1 min. No additional pentane was formed thereafter. After addition of the olefin to solutions of (vi), gas evolution corresponding to 1 mole per mole of (vi) was observed; the $\nu(N_2)$ band of (vi) in the IR spectrum disappeared and no other band attributable to coordinated N_2 was observed.

The amount of pentane formed corresponds to the consumption of all the hydride ligands originally present in (vi) and in (vii) and possibly of some phenyl protons of the ligands.

However, in deuterobenzene solutions of (vi) or (vii) sufficiently concentrated for ^{1}H NMR measurements a weak Co—H signal was observed following the addition of an excess of pentene and the disappearance of the resonances attributed to the hydridic hydrogen of (vi) or (vii). This observation suggests that a new hydridic species was formed, probably by transfer to the Co of a phenyl proton from the ligands. So it seems likely that the isomerization proceeds by addition—elimination.

The fact that the isomerization is second-order in olefin suggests that the rate determining step is the olefin exchange reaction. It seems reasonable that N_2 promotes the isomerization by assisting in the substitution process. Especially if steric hindrance is important in regulating the rate of olefin exchange the influence of N_2 on the exchange reaction is expected to be dependent on the steric configuration of the 2-pentene isomers, so that in the isomerization of 1-pentene the *trans/cis* ratio of the product should be altered by N_2, as is in fact, observed experimentally. It cannot be excluded at this stage of our studies that N_2 affects the addition—elimination step, so that the proposed mechanism must be regarded as tentative.

CONCLUSIONS

The results presented here illustrate the variety of effects which may be produced by molecular nitrogen on coordination catalysis, and point out the difficulties which may be encountered, particularly in kinetic studies, from the practice of performing catalytic reactions routinely under N_2. These results also point out the potential utility of N_2 for the modification of reactivity and selectivity patterns of reactions of hydrocarbons catalyzed by coordination compounds.

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