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Preliminary communication

PROMOTING EFFECTS OF MOLECULAR NITROGEN ON THE ISOMERIZATION OF 1-PENTENE CATALYZED BY HYDRIDODINITROGEN TRIS(TRIPHENYLPHOSPHINE)COBALT

FILIPPO PENNELLA

Phillips Petroleum Company, Research and Development, Bartlesville, Oklahoma 74004 (U.S.A.)

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Summary

The isomerization of 1-pentene to 2-pentene catalyzed by $CoH(N_2)(PPh_3)_3 \cdot Et_2O$ is promoted by molecular nitrogen.

The influence of molecular nitrogen on coordination-catalyzed reactions of olefins is of considerable interest, especially in view of the widespread practice of carrying out such reactions under N_2. We have previously shown [1-3] that N_2 can compete with olefins for coordination to $RuH_2(PPh_3)_3$ and $Ru(PPh_3)_3$ and that consequently N_2 inhibits [2,3] the hydrogenation and the isomerization of pentenes catalyzed by $RuH_4(PPh_3)_3$ and by $RuH_2(N_2)(PPh_3)_3$. We report now a less anticipated effect of N_2 on a catalytic process, the enhancement by N_2 of the double bond isomerization of 1-pentene catalyzed by $CoH(N_2)(PPh_3)_3 \cdot Et_2O$ (I) or $CoH_3(PPh_3)_3$ (II).

The isomerization of 1-pentene to 2-pentene catalyzed by I in toluene,

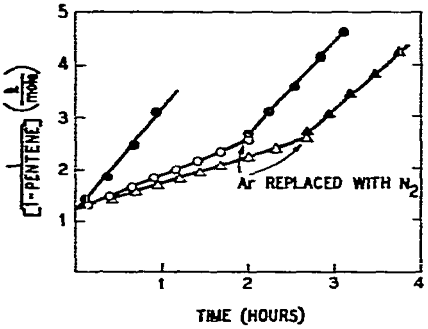


Fig.1. Second-order plot for the isomerization of 1-pentene in toluene at 25 °C and atmospheric pressure catalyzed by $CoH(N_2)(PPh_3)_3 \cdot Et_2O$: ○, under Ar; ●, under N_2. $CoH_3(PPh_3)_3$: △, under Ar; ▲, under N_2; [pentene] = 0.83 mole/l, [Co] = 2.4×10^{-3} mole/l.

or in the absence of solvent, at 25 °C yielded preferentially *cis*-2-pentene. The reaction was promoted by the addition of N_2, and was retarded by the addition of triphenylphosphine. The effects produced by dinitrogen are illustrated in Fig.1, where the isomerization is plotted as a second-order reaction for experiments performed under argon and under dinitrogen. Also shown in Fig.1 are the results obtained in a nitrogen-free system using II as the catalyst, and the effects produced on this system by the addition of N_2. The measured second-order rate constants for these experiments are given in Table 1.

TABLE 1

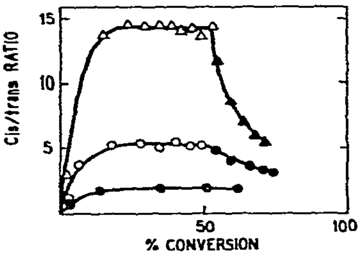
SECOND-ORDER RATE CONSTANTS, K_{obs}, FOR THE ISOMERIZATION OF 1-PENTENE IN TOLUENE AT 25 °C;
[Pentene] = 0.83 Mole/l; [Co] = 2.4 × 10^{-3}Mole/L

Catalyst system	$K_{obs} \times 10^2$ (Mole l^{-1} min)
$CoH(N_2)(PPh_3)_3 \cdot Et_2O$	
Initially under N_2	3.3
$CoH(N_2)(PPh_3)_3 \cdot Et_2O$	
Initially under Ar	1.1
After replacing Ar with N_2	3.1
$CoH_3(PPh_3)_3$	
Initially under Ar	0.9
After replacing Ar with N_2	2.6

In addition to promoting the isomerization of 1-pentene, dinitrogen also affected the isomer distribution in the product, as shown in Fig.2.

The isomerization of *cis*-2-pentene to *trans*-2-pentene catalyzed by I was also enhanced by N_2. Tyrlik [4] 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 (see Fig.3).

Full details will be reported later. The results presented here and those



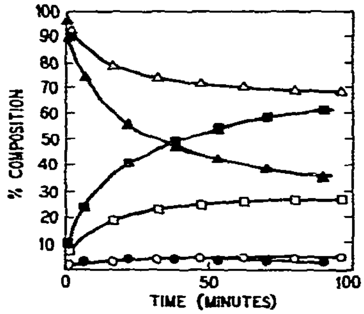


Fig.2. *Cis/trans* isomer ratio in the products of the isomerization of 1-pentene (conditions and symbols as in Fig.1).

Fig.3. Isomerization of *cis*-2-pentene catalyzed by $CoH(N_2)(PPh_3)_3 \cdot Et_2O$ in toluene at 25 °C and atmospheric pressure; [pentene] = 0.83 mole/l; [Co] = 5 × 10^{-3} mole/L. Variation of pentene composition with time; under Ar: ○, 1-pentene; □, *trans*-2-pentene; △, *cis*-2-pentene. under N_2 : ●, 1-pentene; ■, *trans*-2-pentene; ▲, *cis*-2-pentene.

reported previously [2,3] illustrate the variety of effects which may be produced by molecular nitrogen and point out the difficulties which may arise, particularly in kinetic studies, from the practice of performing catalytic reactions routinely under N_2.

References

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