JOURNAL OF CATALYSIS 74, 18–23 (1982)

Structure of Propene in Heterogeneous Catalysis

II. Isomerization of Propene by Atomic Nickel and Magnesium

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Received June 8, 1981; revised October 23, 1981

Unstable π-propene–metal complexes are formed when excess propene is co-condensed with atomic nickel or magnesium. During the formation and decomposition of these complexes, the ligand undergoes a double-bond isomerization by a 1,3-hydrogen shift. Infrared and mass spectroscopic data from $CD_3CH{=}CH_2$/metal complexes show metal-induced, sequential, intramolecular, hydrogen exchange reactions: $CD_3CH{=}CH_2 \rightarrow CH_2DCH{=}CD_2 \rightarrow$ *cis*-$CHD_2CH{=}CHD \rightarrow$ *trans*-$CHD_2CH{=}CHD$. No π-allyl species is observed during these reactions. The low decomposition temperatures of π-propene–nickel and –magnesium complexes (both about −140°C) and the low isomerization activation energies (less than ~0.5 kcal/mol) suggest direct formation of isomerization products from the π-propenes without the intervention of any allyl intermediates. The π-propene may also be the only surface species necessary to account for the products in isomerization, hydrogen exchange, and hydrogenation reactions of propene on zinc oxide catalyst.

INTRODUCTION

An unstable propene–nickel complex formed during the codeposition of excess propene with atomic nickel at liquid nitrogen temperature (*1*) had been shown from its infrared spectrum to be a π-propene–nickel complex that decomposed into metallic nickel and propene at about −140°C (*2*). Earlier, Skell and co-workers (*1*) had suggested that this π-propene complex was undergoing a rapid interconversion with a π-allyl nickel hydride since co-condensation of propene and propene-d_6 led to isotopic scrambling. Although Boenneman (*3*) had reported the π-allyl nickel hydride to be unstable even at −140°C, neither this species nor its stable disproportionation product bis-π-allyl nickel was observed during the previous spectroscopic study (*2*). Thus, the question, whether the spectroscopically observed π-propene complex is a kinetically significant intermediate in such catalytic reactions as olefin double-bond isomerization and hydrogen exchange reactions, still exists and requires an experimental answer. In this report evidence is presented that the π-propene–nickel complex and the unstable propene–magnesium charge-transfer complex both undergo double-bond isomerization by 1,3-hydrogen shift during formation and decomposition of the complexes.

EXPERIMENTAL

All experimental data reported in this study were obtained earlier from infrared spectroscopic investigations of low-temperature propene matrices containing various metal atoms (*2*). The experimental techniques, the low-temperature infrared cell with the metal vaporization unit, the spectroscopic instrumentation, and the sources of chemicals were described in detail before.

RESULTS

The infrared spectrum of π-propene–nickel complex and fundamental vibrational frequencies of nickel complexes of $CH_3CH{=}CH_2$, $CD_3CD{=}CD_2$, and $CD_3CH{=}CH_2$ were presented previously (*2*).

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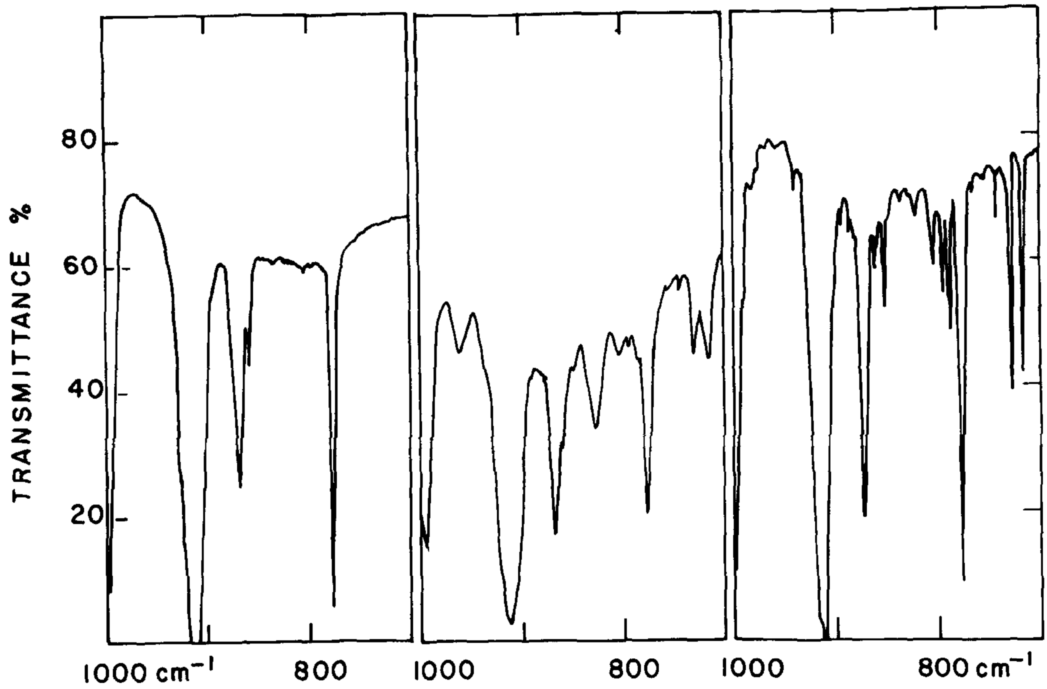

FIG. 1. Infrared spectrum of $CD_3CH{=}CH_2$ at −190°C. Left spectrum: free propene. Middle spectrum: initial spectrum of matrix with nickel atoms. Right spectrum: recovered matrix.

Also, it was shown that the spectrum of the unstable, black, charge-transfer-type, propene–magnesium complex was indistinguishable from that of propene itself. No isotopic dilution, for example, through exchange with traces of water, was evident from the infrared spectrum of $CD_3CD{=}CD_2$ recovered from the experiments. Neither was there evidence of propane formation in the recovered samples of $CD_3CD{=}CD_2$ and $CD_3CH{=}CH_2$.

The exchange reaction between $CH_3CH{=}CH_2$ and $CD_3CD{=}CD_2$ observed earlier by Skell *et al.* (*1*) was not studied here because only partial infrared data on *cis*- and *trans*-$CH_3CH{=}CHD$ by Zerbi *et al.* (*4*) and no data on propene-d_2 were available to assist in the identification of possible exchange products. The partial data on isotopic propenes reported by Dent and Kokes (*5*) were also inadequate for this purpose. However, assignments of the spectrum of $CD_3CH{=}CH_2$ have been reported by Zerbi *et al.* (*4*), by Silvi *et al.* (*6*), and by Abe (*7*). Thus, metal complexes of $CD_3CH{=}CH_2$ were examined in detail for possible hydrogen exchange reactions.

The occurrence of hydrogen exchange reactions in a $CD_3CH{=}CH_2$ matrix containing atomic nickel is clearly evident from the spectra shown in Fig. 1. The left spectrum is from a matrix without any nickel atoms, and its prominent bands at 1000, 913, 872, and 777 cm^{-1} are assigned to the out-of-plane CH wag modes in $-CH{=}$ and $={CH_2}$, the out-of-plane CD_3 wag, and the in-plane CD_3 rock, respectively. The central spectrum in the figure is from an initial scan of a matrix containing nickel atoms, and it shows new bands at 960, 826, 728, and 713 cm^{-1} arising from unstable isotopic π-propene–nickel complexes. The relative intensities of these new bands remained essentially constant as the sample was warmed repeatedly to about −135°C. During these warming cycles the matrix bands at 1000, 913, 872, and 777 cm^{-1} became progressively weaker but recooling of the matrix did not produce any new absorption bands nor changes in relative band intensities. However, enhanced intensities of the 713- and 728-cm^{-1} peaks, as well as the presence of other new bands in the spectrum of the recovered matrix shown on the right of the figure, provide convincing evidence that the hydrogen scrambling reactions had occurred during the formation and the decomposition of the unstable π-propene complex. Whether these hydrogen exchange reactions were inter- or intramolecular processes could not be determined from the infrared data, but mass spectroscopic analyses suggested intramolecular processes to be dominant since no significant amount of $C_3H_2D_4$ was found in the recovered matrix samples or in the original $C_3H_3D_3$ sample.

In the central spectrum of Fig. 1, the 728-cm^{-1} peak is slightly weaker than the 713-cm^{-1} peak, but in the spectrum of the recovered matrix on the right, these relative intensities are reversed. Peak frequencies of these bands in π-propene complex and solid propene as well as in gaseous propene were essentially unchanged. A similar intensity reversal was observed between the matrix collected from decompositions of π-propene complexes at temperatures below about −120°C and the matrix recovered at temperatures from −120°C to room temperature. Consequently, these peaks arise from two different isotopic propene molecules with the 713- and 728-cm^{-1} peaks representing, respectively, the initial and final products of hydrogen exchange reactions. In the carbon double-bond stretch region, the low-temperature infrared spectrum of a recovered propene sample showed in addition to the parent band at 1642 cm^{-1} three new bands at 1622, 1615, and 1606 cm^{-1}. In this case, the relative intensity of the 1622-cm^{-1} peak was much greater than the intensities of other new peaks in the matrix recovered at temperatures above −120°C. The 1622-cm^{-1} band, therefore, must be associated with a final reaction product of the hydrogen scrambling reactions.

According to assignments of the spectrum of propene-d_6 (*4, 6, 7*), the 728- and 713-cm^{-1} bands in the right spectrum of Fig. 1 are in the proper region where the intense CD out-of-plane wag modes should appear. However, since the CD stretch mode band in the functional group $=CD-$ expected near 2250 cm^{-1} was not observed, these bands must arise from the deuterium wag modes in $=CHD$ and $=CD_2$. The 713-cm^{-1} band may be assigned readily to the $=CD_2$ group since the corresponding mode in propene-d_6 appears at 710 cm^{-1}. This leaves the 728-cm^{-1} band to be associated with either the *cis* or *trans* isomer of the $=CHD$ species. The only infrared data on *cis*- and *trans*-$CH_3CH=CHD$ are those reported by Zerbi *et al.* (*4*), but data on *cis* and *trans* isomers of 1,3-butadiene-1-d_1 have been obtained by Abe (*7, 8*). Zerbi *et al.* assigned for the CD wag 800 cm^{-1} (*cis*) and 821 cm^{-1} (*trans*), whereas Abe gave 719 cm^{-1} (*cis*) and 674 cm^{-1} (*trans*). Since the assignments of Abe are generally more consistent with those of Silvi *et al.* (*6*), Abe's choice is adopted here and the 728-cm^{-1} band in the spectrum of the recovered matrix is associated with the *cis* species of the $=CHD$ products. Thus, the observed intensity reversal in the 713- and 728-cm^{-1} bands with decomposition temperatures of the unstable π-propene–nickel complex suggests that $CH_2DCH=CD_2$ is the initial exchange product and *cis*-$CHD_2CH=CHD$ is formed subsequently.

The assignments of three new bands observed in the $C=C$ stretch region impose no difficulty. Both Abe (*7*) and Zerbi *et al.* (*4*) agree that the double-bond stretch frequencies decrease in the order of *trans*-d_1 isomer, *cis*-d_1 isomer, and $-CH=CD_2$ species. Therefore, the frequency assignments are: 1642 cm^{-1} for the parent $CD_3CH=CH_2$, 1622 cm^{-1} for *trans*-$CHD_2CH=CHD$, 1615 cm^{-1} for *cis*-$CHD_2CH=CHD$, and 1606 cm^{-1} for $CH_2DCH=CD_2$. The observed increase in relative intensity of the 1622-cm^{-1} band when π-propene complexes were decomposed at higher temperatures indicates that the final product of hydrogen scrambling reactions is *trans*-$CHD_2CH{=}CHD$. Thus, the exchange sequence is evidently $CD_3CH{=}CH_2 \rightarrow CH_2DCH{=}CD_2 \rightarrow$ *cis*-$CHD_2CH{=}CHD \rightarrow$ *trans*-$CHD_2CH{=}CHD$.

Additional support for the above interpretation, that the principal reaction causing hydrogen exchanges during formation and decomposition of isotopic π-propene–nickel complexes involves a 1,3-shift of hydrogen atoms, comes from a mass spectrum of propene recovered from decomposition of the nickel complex of $CD_3CH{=}CH_2$. According to the data summarized in Table 1, the recovered propene contains a significantly increased fraction of $—CH{=}CHD$ and $—CH{=}CD_2$ species. The greater increase in the relative intensity of the $—CH{=}CHD$ peak compared to that of the $—CH{=}CD_2$ peak is consistent with the conclusion from the infrared data that *cis*- and *trans*-$CHD_2CH{=}CHD$ are formed from the initial product $CH_2DCH{=}CD_2$. Although the mass 30 peak assigned to the $—CD{=}CD_2$ group also shows an increase of a factor of 2, the ratio of relative intensity of this peak to the parent mass 45 peak was 0.10 in the original propene-d_3 sample and 0.078 in the recovered propene.

The magnesium atom complex of propene, which was shown earlier to be an unstable charge-transfer complex (*2*), was also found to isomerize during its formation and decomposition. Propene-d_3 used in the nickel experiments was used again in the magnesium study, but the infrared spectrum of recovered products from the magnesium system showed a substantial increase in isotopically scrambled propenes. The mass spectrum of a recovered sample is also presented in Table 1, and it shows an additional increase in the $—CH{=}CD_2$ species over what was present in the matrix gas from the nickel study. The decrease in relative intensity of the mass 28 peak from the nickel spectrum suggests that subsequent isomerization of $CH_2DCH{=}CD_2$ in the magnesium complex was hindered. The relative intensities of the 728- and 713-cm^{-1} bands in the infrared spectrum of recovered propene also supported this interpretation since the 713-cm^{-1} $=CD_2$ peak increased by 83% whereas the 728-cm^{-1} *cis* $=CHD$ changed by only 50% after complexation with the magnesium atom. Metallic residues from decomposition of the magnesium complex did not cause additional isomerization of propene even after overnight contact with the gas at room temperature.

TABLE 1

Isotopic Composition of $CD_3CH{=}CH_2$ before and after Complexation with Atomic Nickel and Magnesium

Mass number[a]	Assignment	Relative peak intensity		
		Original	Nickel	Magnesium
45	Parent($CD_3CH{=}CH_2$)	1.00[b]	1.00[b]	1.00[b]
44	Parent-H	1.06	1.00	1.26
43	Parent-D	0.80	0.67	1.02
42	Parent-H,D	0.28	0.41	0.63
41	Parent-2D	0.77	0.82	1.16
40	Parent-H,2D	0.65	0.76	0.97
27	Parent($CH{=}CH_2$)	1.00[b]	1.00[b]	1.00[b]
28	$CH{=}CHD$	0.59	1.64	1.02
29	$CH{=}CD_2$	0.32	0.58	0.79
30	$CD{=}CD_2$	0.085	0.15	0.23

[a] Data from Extranuclear Quadrupole Type II mass spectrometer operating at 100 V ionization energy.
[b] Used as reference mass peak.

DISCUSSION

Nickel and magnesium atoms have been shown to induce isomerization of propene by 1,3-hydrogen shift. This isomerization occurred only during formation and decomposition of the π-propene–nickel complex or the charge-transfer-type propene–magnesium complex. Since both complexes decomposed near −140°C, their zero-point energies must be fairly close to the top of the potential energy barrier in the reaction path leading to the isomerization products. If the thermal energy at −140°C is taken as a measure of the isomerization activation energy, then the difference in energy between the reactants and the transition state is likely to be smaller than about 0.5 kcal/mol. Since no π-allyl nickel hydride nor bis-π-allyl nickel was detected during the isomerization by nickel, the observed π-propene must go directly to the reaction product without the formation of an allyl intermediate. A similar conclusion is reasonable for the magnesium case also. Thus, the unstable π-propene complexes are indeed the kinetically significant intermediate in the isomerization of propene by nickel and magnesium atoms.

Both a π-allyl and a π-propene species had been identified by Dent and Kokes (*5, 9*) in the infrared spectra of isotopic propenes adsorbed on zinc oxide catalyst. The π-propene was a weakly bonded surface species characterized by a single new infrared band at 1620 cm^{-1}, but the anionic (*10*) π-allyl species was strongly adsorbed and required an evacuation time of 1.5 h at 125°C for its complete removal (*5*). From the infrared data (*5, 9*) and subsequent microwave analysis of products from hydrogen exchange and hydrogenation reactions, Naito *et al.* (*11*) and Kokes and co-workers (*9, 12*) concluded that the π-allyl anion was the intermediate in the isomerization and hydrogen exchange reactions but the intermediate in the hydrogenation reaction was the π-propene species. However, according to the results from the present study, all three reactions can have a common intermediate, namely, the π-propene surface species. In this case, the existing experimental data may be interpreted equally well in terms of the following elementary steps for surface reactions taking place on zinc oxide:

$$C_3H_6 + ZnO \rightleftharpoons \pi\text{-}C_3H_6 \cdot ZnO, \quad (1)$$

$$\pi\text{-}C_3H_6 \cdot ZnO \rightleftharpoons (Zn^{2+}\pi\text{-}C_3H_5^{-}\,OH^{-}), \quad (2)$$

$$\pi\text{-}C_3H_6 \cdot ZnO + D_2 \rightleftharpoons \pi\text{-}C_3H_5D \cdot ZnO + HD, \quad (3)$$

$$\pi\text{-}C_3H_6 \cdot ZnO + D_2 \rightarrow C_3H_6D_2 + ZnO. \quad (4)$$

Reaction (1) in the above mechanism is a slightly exothermic reversible formation of the weakly bonded surface π-propene species, and it corresponds to the formation of the π-propene species observed at low temperatures in the atomic nickel and magnesium systems in the present study. During the forward and reverse steps in this reaction, double-bond isomerization by 1,3-hydrogen shift can occur. The exothermic reaction (*2*) merely serves as a sink for propene in this mechanism. This reaction was absent in the nickel and magnesium systems of the present study. Reactions (3) and (4) represent, respectively, the reversible hydrogen exchange and an irreversible hydrogenation reaction. Equivalent reactions in the π-propene–nickel system were not studied here, but Skell *et al.* (*1*) had reported that treatment of the nickel complex with D_2O gave some deuterated propenes and propanes. Also, direct spectroscopic examination of recovered products from π-propene–nickel complex decomposed in the presence of D_2 indicated that reactions equivalent to steps (3) and (4) can also take place in the atomic nickel system (*13*).

REFERENCES

1. Skell, P. S., Havel, J. J., Williams-Smith, D. C., and McGlinchey, M. J., *J. Chem. Soc. Chem. Commun.*, 1098 (1972).

2. Hisatsune, I. C., *J. Catal.* **73,** 9 (1982).
3. Boenneman, H., *Angew. Chem. Int. Ed. Engl.* **9,** 736 (1970).
4. Zerbi, G., Peraldo, M., and Mantica, E., *in* "Proceedings, Internat. Symposium Molec. Struc. and Spectrosc., Tokyo, Japan, 1962," paper C-213.
5. Dent, A. L., and Kokes, R. J., *J. Amer. Chem. Soc.* **92,** 6709 (1970).
6. Silvi, B., Labarbe, P., and Perchard, J. P., *Spectrochim. Acta Part A* **29,** 263 (1973).
7. Abe, K., Ph.D. thesis, Faculty of Science, The University of Tokyo, Japan, 1970.
8. Shimanouchi, T., "Tables of Molecular Vibrational Frequencies Consolidated Volume I," NSRDS-NBS 39, U.S. Dept. of Commerce, Washington, D.C., 1972.
9. Dent, A. L., and Kokes, R. J., *J. Amer. Chem. Soc.* **92,** 6718 (1970).
10. Nguyen, T. T., and Sheppard, N., *J. Chem. Soc. Chem. Commun.*, 868 (1978).
11. Naito, S., Kondo, T., Ichikawa, M., and Tamaru, K., *J. Phys. Chem.* **76,** 2184 (1972).
12. Chang, C. C., Conner, W. C., and Kokes, R. J., *J. Phys. Chem.* **77,** 1957 (1973).
13. Bandow, H., Onishi, T., Tamaru, K., and Hisatsune, I. C., unpublished work; Bandow, H., Ph.D. thesis, Faculty of Science, The University of Tokyo, 1978.