JOURNAL OF CATALYSIS **75**, 425–427 (1982)

Isomerization of Butenes by Atomic Nickel and Magnesium

An earlier infrared spectroscopic study of low-temperature propene matrices prepared by codeposition with atomic nickel or magnesium showed that unstable π-propene complexes of these metal atoms are trapped and that during formation and decomposition of these complexes propene is isomerized by intramolecular 1,3-hydrogen exchange (*1*). The present note reports the formation of similar π-complexes of butenes and their isomerizations.

An infrared spectrum of *trans*-butene matrix containing atomic nickel at liquid nitrogen temperature is shown in Fig. 1 (upper curve). Two sets of new absorption bands due to the *cis*-isomer and an unstable π-complex are identified in this spectrum. Neither of these sets of peaks was present in the spectrum of *trans*-butene matrix without nickel atoms. Slow warning caused the brown matrix to become colorless at about −150°C and concomitantly absorption bands due to the π-complex became more intense. Near −120°C *trans*-butene started to sublime from the low-temperature window leaving only the π-complex. During this warming sequence there was no increase in absorption bands of the *cis*-isomer. The π-complex itself started to decay at about −110°C leaving only metallic nickel on the sample window. The spectrum of the recovered matrix recondensed at liquid nitrogen temperature is shown in Fig. 1 (lower curve). Additional *cis*-butene and a small amount of 1-butene (910 cm^{-1}) were formed during the decomposition of the π-complex.

Fractional sublimation of a *trans*-butene matrix containing nickel atoms and recooling to liquid nitrogen temperature permitted infrared bands of an unstable π-complex of *trans*-butene and atomic nickel to be identified at 2960, 2935, 2900, 2850, 1438, 1370, 1238, 1027, 966, 847, 374, and 330, all in cm^{-1} units. As in the case of π-propene (*1*), this spectrum was distinct from those of allylic forms of butene (*2, 3*) but was very similar to the spectrum of the butene analog of Zeise's salt K (*trans*-$C_4H_8PtCl_3$). According to Hiraishi *et al.* (*4*), the triangular PtC_2 group in the latter π-complex has ν(C–C) = 1263 cm^{-1}, ν(Pt–C, antisymmetric) = 491 cm^{-1}, and ν(Pt–C, symmetric) = 386 cm^{-1}. The corresponding modes in the present nickel complex may be taken to be 1238, 374, and 330 cm^{-1}, respectively.

Spectra of initial and recovered matrix of *cis*-butene with atomic nickel is shown in Fig. 2. In this case, only the formation of a π-complex was apparent in the initial spectrum. Although the most intense *trans*-butene band at 970 cm^{-1} was overlapped by a *cis*-isomer band, the sharp peak of *trans*-butene at 1060 cm^{-1} was absent initially. In the spectrum of the recovered matrix, not only were the *trans*-butene absorption bands prominent but the strongest band of 1-butene at 910 cm^{-1} was readily identifiable. A sharp weak peak at 728 cm^{-1} due to butane was also present.

Cis-butene matrices began to sublime from the sample window at about −140°C, and the π-complex decomposition became appreciable near −120°C. Strong absorption bands of this complex were identified at 2960, 2930, 2893, 2848, 1435, 1366, 1218, 1018, 970, 848, 680, and 360 in cm^{-1} units. This spectrum resembled closely that of π-butene in K (*cis*-$C_4H_8PtCl_3$) (*4*).

The 1-butene complex was the least stable among π-butene complexes of nickel, and it began to decay at about −150°C where the matrix itself started to sublime from the window. The major peaks of this complex were at 2950, 2920, 2860, 1445, 1360, 1227, 1057, 992, 964, 905, 840, 780, 636, 430, 400, 388, and 368 in cm^{-1} units. Although the spectrum of Zeise's salt analog of this complex has not been reported, the presence of characteristic bands at

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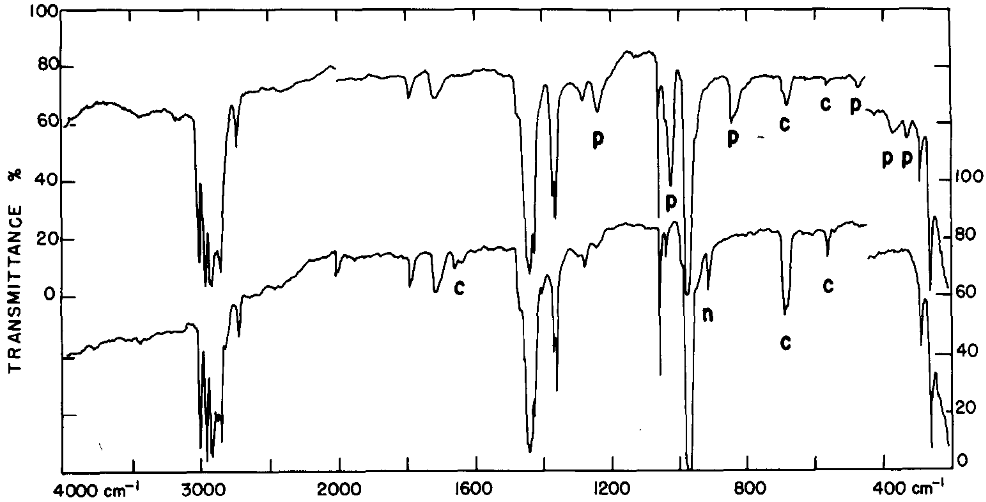

FIG. 1. Infrared spectra of *trans*-butene/nickel system at liquid nitrogen temperatures: upper spectrum = initial sample, lower spectrum = recovered sample, p = π-complex, c = *cis*-butene, n = 1-butene.

1227, 388, and 368 cm^{-1} suggests that the nickel complex is also a π-complex. Overlapping bands prevented the identification of *trans*-butene in the initial spectrum and in the spectrum of recovered matrix, but these spectra showed that only traces of *cis*-isomer were produced during formation and decomposition of the π-complex. However, 1-butene gas was isomerized extensively when it was in contact at room temperature overnight with metallic nickel deposited on the infrared window by the decomposition of the π-complex.

Butene matrices containing atomic magnesium were almost black, but their infrared spectra were indistinguishable from those of pure matrices. Warming of these matrices produced no new absorption

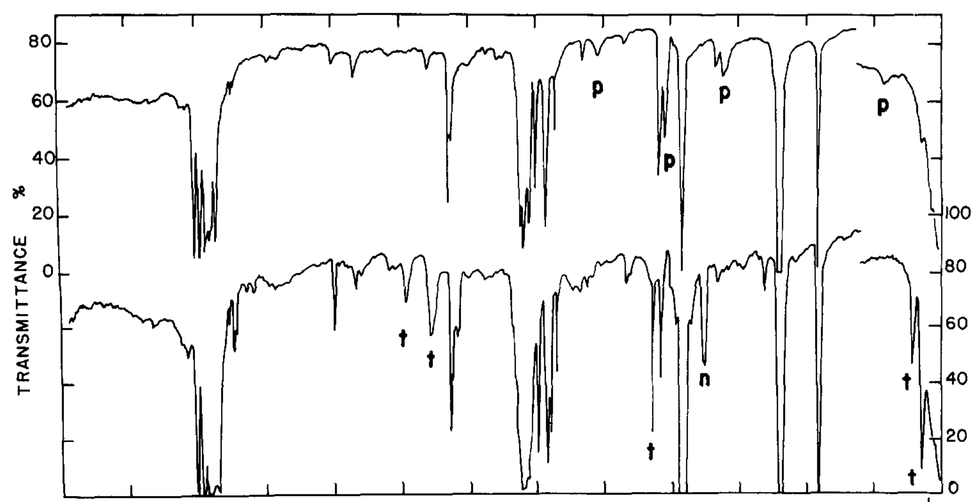

FIG. 2. Infrared spectra of *cis*-butene/nickel system at liquid nitrogen temperature: upper spectrum = initial sample, lower spectrum = recovered sample, p = π-complex, t = *trans*-butene, n = 1-butene.

bands, and sublimation of samples did not appear to be affected by the presence of magnesium atoms. Nevertheless, comparison of spectra of initial and recovered matrices showed that *trans*-butene was isomerized into *cis*- and 1-butene to about the same extent as with nickel atoms. No isomerization was observed, however, in a *cis*-butene matrix. Even when gaseous *cis*-butene was exposed overnight at room temperature to magnesium residues on the cell window, no absorption bands due to 1-butene nor to *trans*-butene were detected in the low-temperature spectrum of the sample. Also, only the *cis*-isomer was formed in 1-butene matrix with magnesium atoms.

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Received September 23, 1981; revised December 29, 1981