Stereoselectivity in the Metathesis Reaction of But-2-ene on a β-Titanium Oxide-supported Molybdenum Oxide

By KATSUMI TANAKA,* KEN-ICHI TANAKA,† and KOSHIRO MIYAHARA

(*Research Institute for Catalysis, Hokkaido University and* †*Faculty of Engineering, Hokkaido University, Sapporo* 060, *Japan*)

Summary With MoO_x/β-TiO_2 as catalyst the stereoselective formation of *cis*- and *trans*-[$^2H_4$]but-2-ene is observed in the metathesis of equimolar mixtures of *cis*-[$^2H_0$]- and -[$^2H_8$]but-2-ene, and *trans*-[$^2H_0$]- and -[$^2H_8$]-but-2-ene, respectively, the yields of *cis*- and *trans*-but-2-ene from reactions of the corresponding pent-2-ene isomers are in good agreement, but metathesis of propene selectively yields *trans*-but-2-ene

METAL carbene and metallocyclobutane intermediates have been generally accepted for olefin metathesis reactions especially in homogeneous systems,[1] however, the process leading to initial formation of metal carbenes[2] and the *cis–trans* stereoselectivity in the olefins produced[3] still constitute interesting problems We now report the stereoselectivity observed in [$^2H_4$]but-2-ene ($CH_3CH{=}CDCD_3$) or [$^2H_0$]but-2-ene formation on a novel catalyst, MoO_x/β-TiO_2 ($2{\cdot}9 > x > 2{\cdot}3$),[4] on which the olefin metathesis reaction took place with neither intermolecular hydrogen scrambling nor isomerization through alkyl or carbonium ion intermediates [4,5] The reaction was carried out over 0·3 g of 6·7 wt% of MoO_x/β-TiO_2 catalyst in a closed circulation system of *ca* 350 ml volume

trans-But-2-ene consisting of [$^2H_0$]-, [$^2H_4$]-, and [$^2H_8$]-isomers and *cis*-[$^2H_4$]but-2-ene were formed in the reaction of a 1:1 mixture of *cis*-[$^2H_0$]- and *cis*-[$^2H_8$]-but-2-ene. The figure shows that only the [$^2H_0$]-, [$^2H_4$]-, and [$^2H_8$]-but-2-enes were formed in this reaction, and we conclude that the *trans*-but-2-ene is formed by the metathesis reaction on the MoO_x/β-TiO_2 catalyst [4,5] The [$^2H_4$]but-2-ene was composed of more than 60% of the *cis* form at the initial stage of the reaction, and the *cis/trans* ratio of the [$^2H_4$]but-2-ene decreased to reach an equilibrium value as the reaction proceeded In contrast, *trans*-[$^2H_4$]but-2-ene was produced with high selectivity in the early stages of

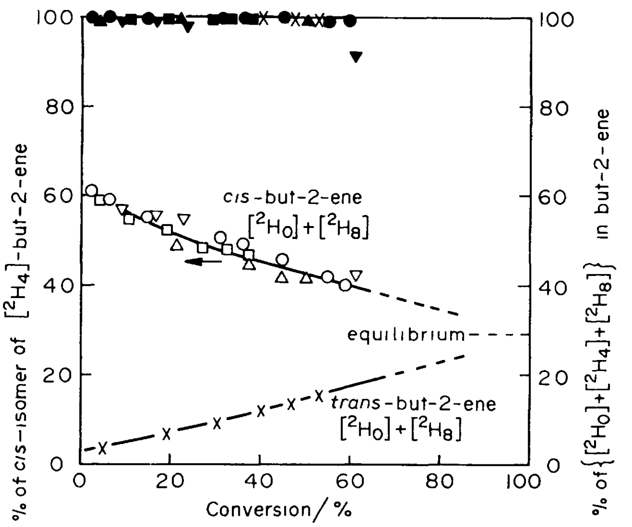

FIGURE Metathesis reaction of a 1:1 mixture of [$^2H_0$]- and [$^2H_8$]-but-2-ene on an MoO_x/β-TiO_2 catalyst ○, ● −10 °C, 32 2 mmHg total pressure, □, ■ −8 °C, 8 7 mmHg, △,▲ 25 °C, 4 5 mmHg, ▽, ▼ 25 °C, 37 5 mmHg, × 25 °C, 23 2 mmHg Open symbols, % of *cis*-isomer, filled symbols, % of {[$^2H_0$] + [$^2H_4$] + [$^2H_8$]} Equilibrium conversion, 100%

the metathesis reaction of a 1 : 1 mixture of *trans*-[$^2H_0$]- and *trans*-[$^2H_8$]-but-2-ene. These results indicate that the *cis* or *trans* geometry of the starting material was largely retained in the [$^2H_4$]but-2-ene produced in the degenerate metathesis reaction of but-2-ene. This stereoselectivity is attributed to stability differences between the metallocyclobutane intermediates with various symmetries.[3d,f,g]

The productive metathesis reaction of pent-2-ene on this MoO_x/β-TiO_2 catalyst revealed the same degree of stereoselectivity in but-2-ene formation as that in the degenerate metathesis reaction of but-2-ene mentioned above. However, the *cis/trans* ratio was 0·2 for but-2-ene produced in the early stages of the metathesis reaction of propene on the present catalyst.

(*Received*, 24*th March* 1980; *Com.* 306.)

[1] *E.g.* J. J. Rooney and A. Stewart, in 'Catalysis' (Specialist Periodical Reports), vol. 1, ed. C. Kemball, The Chemical Society, 1977, ch. 8.

[2] N. J. Cooper and M. L. H. Green, *J. Chem. Soc., Chem. Commun.*, 1974, 761; E. L. Muetterties, *Inorg. Chem.*, 1975, **14**, 951; J. I. C. Archibald, J. J. Rooney, and A. Stewart, *J. Chem. Soc., Chem. Commun.*, 1975, 547; M. Ephritikhine, M. L. H. Green, and R. E. Mackenzie, *ibid.*, 1976, 619.

[3] (a) W. B. Hughes, *J. Chem. Soc., Chem. Commun.*, 1969, 431; *J. Am. Chem. Soc.*, 1970, **92**, 532; (b) A. I. Milanovic, J. M. Basset, H. Praliaud, M. Dufaux, and L. De Mourgues, *J. Catal.*, 1973, **31**, 408; (c) T. Okuhara and K. Tanaka, *ibid.*, 1976, **42**, 474; (d) J. L. Bilhou, J. M. Basset, R. Mutin, and W. F. Craydon, *J. Am. Chem. Soc.*, 1977, **99**, 4083; (e) C. P. Casey and H. E. Tuinstra, *ibid.*, 1978, **100**, 2270; (f) M. Leconte and J. M. Basset, *ibid.*, 1979, **101**, 7296; (g) K. Tanaka, Ph.D. thesis, Hokkaido Univ., 1980.

[4] K. Tanaka, K. Tanaka, and K. Miyahara, *Shokubai*, 1979, **21**, 73P.

[5] K. Tanaka, K. Tanaka, and K. Miyahara, *J. Chem. Soc., Chem. Commun.*, 1979, 314.