The Ethylidene Route as the Predominant Path for the Degenerate Metathesis of Propene

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Experiments using a 1 : 1 : 1 : 1 mixture of [$^2H_0$]- and [$^2H_6$]-propene, [$^{13}C_0$]- and [$^{13}C_2$]-ethene provide conclusive evidence that the ethylidene route is the predominant path for the degenerate metathesis of propene on $MoO_3/TiO_2/SnMe_4$ or $MoO_{3-x}/TiO_2/SnMe_4$ catalysts.

The metal alkylidene and metallacyclobutane mechanism[1] for alkene metathesis leads to the conclusion that the productive metathesis of propene giving ethene and but-2-ene is brought about by alternative reactions of propene with ethylidene and methylidene intermediates as described by reaction (i) in Scheme 1. However, the interesting problem of the kind of active alkylidene species for the degenerate metathesis of propene still remains because the degenerate reaction can take place through the reaction of propene with either $M{=}CH_2$ (route III in Scheme 1) or $M{=}CHCH_3$ (route IV in Scheme 1). So far only two major attempts have been made to clarify the predominant propagating species for the degenerate metathesis of alk-1-enes.[2,3] Here it is reported that the ethylidene route is the dominant reaction path in the degenerate metathesis of propene.

In these experiments, special catalysts which were developed by us,[4] MoO_3/ and MoO_{3-x}/TiO_2 treated with $SnMe_4$, were adopted. These catalysts are quite active for alkene metathesis but less active for hydrogen scrambling or double bond migration in alkenes. Thus, meaningful metathesis experiments with ^2H as a label can be carried out. When an equimolar mixture of [$^2H_0$]- and [$^2H_6$]-propene was allowed to

(i) C=C–C + C=C–C ⟶ C=C + C–C=C–C

				(*m*/*z* = 28)	
(1)	M=C + C=C–C	⟶	M=C–C + C=C		I
(2)	M=C + *C=*C–*C	⟶	M=*C–*C + C=*C	(30)	
(3)	M=*C + C=C–C	⟶	M=C–C + *C=C	(30)	
(4)	M=*C + *C=*C–*C	⟶	M=*C–*C + *C=*C	(32)	
(5)	M=C–C + C=C–C	⟶	M=C + C–C=C–C	(56)	II
(6)	M=C–C + *C=*C–*C	⟶	M=*C + C=C–*C–*C	(60)	
(7)	M=*C–*C + C=C–C	⟶	M=C + *C–*C=C–C	(60)	
(8)	M=*C–*C + *C=*C–*C	⟶	M=*C + *C–*C=*C–*C	(64)	

(ii) C=C–C + *C=*C–*C ⟶ *C=C–C + C=*C–*C

(9)	M=*C + C=C–C	⟶	M=C + *C=C–C	(44)	III
(10)	M=C + *C=*C–*C	⟶	M=*C + C=*C–*C	(46)	
(11)	M=*C–*C + C=C–C	⟶	M=C–C + C=*C–*C	(46)	IV
(12)	M=C=C + *C=*C–*C	⟶	M=*C–*C + *C=C–C	(44)	

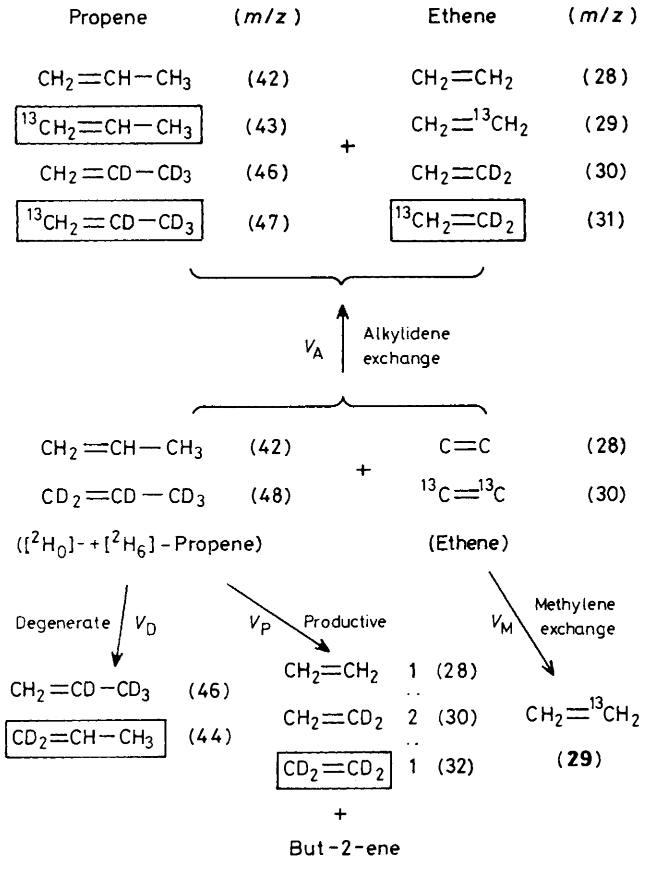
(iii) C=C–C + ^{13}C=^{13}C ⟶ ^{13}C=C–C + C=^{13}C

(13)	M=C + C=C–C	⟶	M=C–C + C=C	(28)	I
(14)	M=C + *C=*C–*C	⟶	M=*C–*C + C=*C	(30)	
(15)	M=^{13}C + C=C–C	⟶	M=C–C + ^{13}C=C	(29)	
(16)	M=^{13}C + *C=*C–*C	⟶	M=*C–*C + ^{13}C=*C	(31)	
(17)	M=C + C=C–C	⟶	M=C + C=C–C	(42)	III
(18)	M=C + *C=*C–*C	⟶	M=*C + C=*C–*C	(46)	
(19)	M=^{13}C + C=C–C	⟶	M=C + ^{13}C=C–C	(43)	
(20)	M=^{13}C + *C=*C–*C	⟶	M=*C + ^{13}C=*C–*C	(47)	
(21)	M=C–C + C=C	⟶	M=C + C=C–C	(42)	V
(22)	M=C–C + ^{13}C=^{13}C	⟶	M=^{13}C + ^{13}C=C–C	(43)	
(23)	M=*C–*C + C=C	⟶	M=C + C=*C–*C	(46)	
(24)	M=*C–*C + ^{13}C=^{13}C	⟶	M=^{13}C + ^{13}C=*C–*C	(47)	

(iv) C=C + ^{13}C=^{13}C ⟶ C=^{13}C + ^{13}C=C

(25)	M=C + C=C	⟶	M=C + C=C	(28)	VI
(26)	M=C + ^{13}C=^{13}C	⟶	M=^{13}C + C=^{13}C	(29)	
(27)	M=^{13}C + C=C	⟶	M=C + ^{13}C=C	(29)	
(28)	M=^{13}C + ^{13}C=^{13}C	⟶	M=^{13}C + ^{13}C=^{13}C	(30)	

Scheme 1



Scheme 2

react, ethylene and but-2-ene were formed by productive metathesis, and at the same time [$^2H_2$]- and [$^2H_4$]-propene were formed by the degenerate reaction. It was confirmed that the degenerate metathesis of propene proceeds 10 to 27 times faster than the productive metathesis.[4] If a 1 : 1 : 1 : 1 mixture of [$^2H_0$]- and [$^2H_6$]-propene, [$^{13}C_0$]- and [$^{13}C_2$]-ethene is contacted with the catalysts (0.1—0.2 g) mounted in a closed circulation system of about 260 ml, four types of metathesis reactions occur simultaneously as shown in Scheme 1, (i)—(iv), where *C indicates the deuterium labelled carbon and the number in parenthesis represents the mass number (m/z) of the alkene obtained. In this way, we can monitor all possible elementary reaction steps simultaneously by measuring isotope labelled alkenes. The degenerate metathesis reaction of propene indicated by reaction (ii) corresponds to route III or route IV in Scheme 1. On the other hand, the alkylidene exchange metathesis (so-called cross metathesis) described by the reaction (iii) is caused by routes I, III, and V in Scheme 1. Here it is worth noting that in the above akylidene carrying steps, methylidene species from propene participate in the degenerate metathesis [steps (9) and (10)] while those from ethene participate in the alkylidene exchange metathesis [(17), (18), (19), and (20)]. The productive metathesis of propene, reaction (i), is brought about by route I and route II, while reaction (iv) occurs through route VI in Scheme 1. The isotopically labelled alkenes produced by the reactions (i)—(iv) are summarized in Scheme 2.

Table 1. Relative metathesis rates on MoO_3/ and MoO_{3-x}/TiO_2 activated with $SnMe_4$.

	ν_D	:	ν_A	:	ν_P	:	ν_M
$MoO_3/TiO_2/SnMe_4$[a]	10	:	2	:	1	:	0.2
$MoO_{3-x}/TiO_2/SnMe_4$[b]	27	:	2	:	1	:	0.2

[a] Catalyst; 0.2 g treated with $SnMe_4$ (2 Torr), propene (11.6 Torr), ethene (10.3 Torr). [b] Catalyst; 0.1 g treated with $SnMe_4$ (1Torr), propene (15.4 Torr), ethene (15.5 Torr).

In these experiments, each metathesis step could be distinguished by measuring non-overlapping mass numbers of alkenes such as those surrounded by squares in Scheme 2, that is, 1,2-[$^2H_2$]-propene (m/z = 44) for the degenerate metathesis of propene, [$^2H_4$]-ethene (m/z = 32) or but-2-ene for the productive metathesis, 1-[$^{13}C_1$]-propene (m/z = 43) and 1-[$^{13}C_1$]-2,3,3,3-[$^2H_4$]-propene (m/z = 47) or [$^{13}C_1$]-1,2-[$^2H_2$]-ethene (m/z = 31) for the alkylidene exchange metathesis. The ethene exchange metathesis described by equation (iv) was evaluated by the difference in the amount of [$^{13}C_1$]-ethene (m/z = 29) and [$^{13}C_1$]-1,2-[$^2H_2$]-ethene (m/z = 31). Relative rates for each metathesis step are summarized in Table 1, where, ν_P, ν_D, ν_A, and ν_M are the initial rates for the productive (i), degenerate (ii), alkylidene exchange (iii), and methylidene (ethene) exchange (iv) metathesis reactions, respectively. The turnover frequencies for the productive metathesis reaction of propene were 9.3×10^{-5} and 5.4×10^{-4} on MoO_3/ and $MoO_{3-x}/TiO_2/SnMe_4$ catalysts, where all Mo atoms were assumed to participate in the reaction. It is worthy of note that ν_D is 5 to 14 times larger than ν_A which is responsible for the routes I, III, and V in Scheme 1. Consequently, it can be concluded that the ethylidene route (route IV) predominates for the degenerate metathesis of propene.

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