Mechanism for Initial Carbene Formation in Olefin Metathesis over Fixed Mo Catalysts

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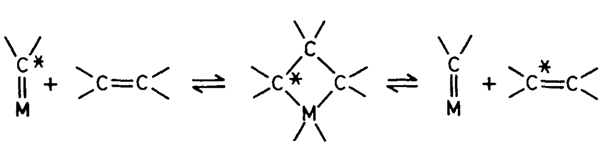
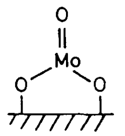
It is indicated that the initial carbene for ethene or propene metathesis over active fixed Mo catalysts with well defined reaction sites is formed by a 1,2-hydrogen shift *via* a molybdenum–n-alkenyl intermediate.

Much effort has been devoted to the elucidation of the mechanism of metathesis since the original work of Banks and Bailey in 1964.[1] A carbene chain mechanism *via* a metallacyclobutane intermediate (**2**) is currently accepted for olefin metathesis with both homogeneous and heterogeneous catalysts (Scheme 1).[2] However, the way in which the carbene (**1**) (initiator for

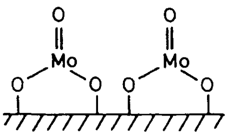


(1) (2)

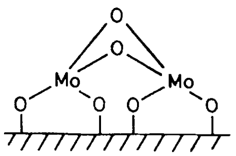
Scheme 1



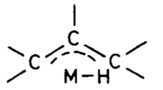
(A)



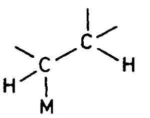
(B)



(C)



(3)



(4)

the chain reaction) is formed on heterogeneous oxide catalysts containing no carbene sources remains to be resolved; three possible mechanisms have been proposed: (a) formation of the η^3-allyl complex (**3**) by allylic hydrogen elimination to give a metallacyclobutane intermediate as demonstrated by Green *et al.*,[3] (b) intramolecular 1,2-hydrogen transfer to give an alkylidene complex as suggested by Fischer *et al.*,[4] and (c) formation of the half-hydrogenated alkyl complex (**4**) by hydrogen addition to the olefin from a surface metal hydride, followed by α-hydrogen elimination as proposed by Laverty *et al.*[5] We now report initial carbene formation by a 1,2-hydrogen shift *via* alkenyl (ethenyl or prop-1-enyl) intermediates for ethene or propene metathesis over active fixed Mo catalysts.

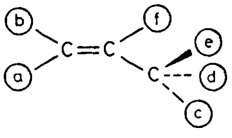
The fixed Mo catalysts which have the well defined structures (A)—(C) were synthesized *via* the reaction between Mo(η^3-C_3H_5)$_4$ or Mo_2(η^3-C_3H_5)$_4$ and surface OH groups of alumina, followed by chemical treatment. The quantities of Mo fixed on the samples Al_2O_3-1 (surface area 190 m^2 g^{-1}) or Al_2O_3-2 (385 m^2 g^{-1}) were 0.25—1.98 wt% (Mo/Al_2O_3). The surface Mo species have been demonstrated to be distributed uniformly and molecularly (*ca.* 100%).[6,7] The fixed catalysts with co-ordinatively unsaturated Mo^{IV} ions showed high catalytic activities for propene metathesis at 266—308 K (2 CH_2=$CHCH_3$ $\rightleftharpoons$ CH_2=CH_2 + CH_3CH=$CHCH_3$). The turnover frequencies (t.f., 10^{-3} s^{-1}) at 273 K and 2.5 kPa of C_3H_6 were found to be 3.97, 7.18, 2.10, and 5.42 for (A)/Al_2O_3-1, (A)/Al_2O_3-2, (B)/Al_2O_3-1, and (C)/Al_2O_3-2, respectively. The t.f. for each catalyst was independent of the Mo concentration, indicating that the properties of the individual Mo ions in the fixed catalysts were uniform. The products of the reactions were identified by microwave spectroscopy (including the positions of deuteriation).

The initial rates of propene metathesis [d(ethene)/d*t*] over the active fixed Mo catalysts with uniform reaction sites were found to depend upon the position of deuteriation of the deuteriopropene (Table 1). The initial rate of metathesis of CH_2=$CHCD_3$ was almost same as that for CH_2=$CHCH_3$ and the rate for CH_2=$CDCH_3$ was slightly lower, whereas large kinetic isotope effects were observed in the metathesis of CD_2=$CHCH_3$ or CD_2=$CDCD_3$. These large isotope effects are not due to the translational term in the rate equation. When C_3H_6 or C_3D_6 was admitted onto a surface on which carbene species had been produced in advance by C_3H_6 (or also C_3D_6 equally) metathesis, their metathesis rates were approximately the same; this implies that the hydrogen isotope effects are associated with the first step of the metathesis, that is, the formation of the initial carbene. Thus Table 1 indicates that the breaking of a carbon–hydrogen bond of the methylene group, not the methyl group, of a propene molecule must be involved in the initial stage of the reaction sequence. Elimination of methylene hydrogen atoms was also indicated by the hydrogen exchange between C_3H_6 and C_3D_6 under the metathesis conditions (Table 2). The hydrogen atoms of the methylene group [a and b in structure (X)] were exclusively dissociated and exchanged on the Mo sites (this was negligible on the Al_2O_3 support under similar conditions), whereas exchange of the other hydrogen atoms (c—f) was not observed after 2 min reaction. The mechanism of this exchange is not clear at present but if the uniformity of the Mo sites is taken into account, the eliminated hydrogen atom seems to have some residence time to allow hydrogen exchange with another propene molecule before 1,2-hydrogen transfer on the co-ordinatively unsaturated Mo^{IV} metathesis sites. It is to be noted that the active Mo catalysts provide almost selective methylene-hydrogen exchange.

Table 1. Kinetic isotope effects in propene metathesis at 273 K.[a]

Deuterio-propene	Surface structure/support (A)/Al_2O_3-1	(A)/Al_2O_3-2	(C)/Al_2O_3-2
CH_2=$CHCD_3$	0.96	0.96	1.02
CH_2=$CDCH_3$	0.92	0.93	1.00
CD_2=$CHCH_3$	0.65	0.62	0.65
CD_2=$CDCD_3$	0.61	0.60	0.62

[a] Relative ratios of initial rates of deuteriated-propene metathesis to that of C_3H_6 metathesis.



(X)

The metathesis of ethene, which cannot generate η^3-allyl species (CH_2=CH_2 + CD_2=CD_2 $\rightleftharpoons$ 2 CH_2=CD_2) proceeded on the Mo catalyst† as shown in Table 2. The t.f. for the (A)/Al_2O_3-1 catalyst was 3.4 × 10^{-3} s^{-1} at 298 K and 5.7 kPa. Again ethene metathesis was accompanied by hydrogen exchange ([$^2H_1$]- and [$^2H_3$]-species). Thus the present microwave and mass spectroscopic studies exclude mechanism (a) involving allylic hydrogen elimination.

Propene metathesis was not significantly enhanced by H_2 addition. When a mixture of C_3D_6 and H_2 was admitted onto the catalyst, hydrogen was not incorporated in the metathesis products (C_2D_4 and C_4D_8) and the parent C_3D_6 in the initial stage of metathesis. It is clear that surface hydrogen atoms originally retained on the catalyst or derived from added H_2 had no important role in metathesis. Mechanism (c) *via* a half-hydrogenated propyl species is very unlikely.

On the basis of the present tracer studies over the active fixed Mo catalysts with well defined reaction sites the formation of the carbene complex (**7**) from ethene or propene may

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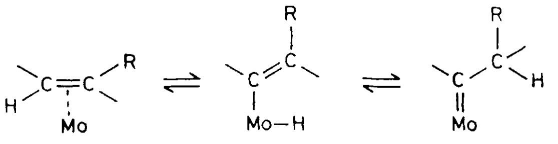
† Homologation of ethene to form propene over the fixed Mo^{IV} catalyst took place only above 343 K.

Table 2. Hydrogen exchange and degenerative metathesis of ethene (298 K) or propene (273 K) over the fixed Mo catalyst [(A)/Al_2O_3-1].[a]

Reactant	Reaction time/min	$^2H_1$ distribution/%[b]				$^2H_2$ distribution/%[b]		
		a	b	$\underbrace{\text{c, d, and e}}$	f	a, b	$\underbrace{\text{a, d and a, f}}$	$\underbrace{\text{c, d and c, f}}$
C_3H_6 + C_3D_6	2	53.8	46.2	0	0	100	0	0
	15	45.4	39.6	3.5	4.5	100	Trace	0

Reactant	Reaction time/min	Deuteriated ethane/%				
		$^2H_0$	$^2H_1$	$^2H_2$	$^2H_3$	$^2H_4$
C_2H_4 + C_2D_4	15	25.4	12.9	24.5	11.4	25.8
	30	17.6	16.0	32.1	16.9	17.4

[a] Catalyst, 0.22 g; Mo/Al_2O_3, 1.98 wt%; C_3H_6 = C_3D_6 = 3.0 kPa; C_2H_4, 2.8 kPa; C_2D_4, 2.9 kPa. [b] For lettering see structure (X); d = e.



(5) (6) (7)

Scheme 2

be well represented by the mechanism in Scheme 2 *via* a molybdenum-n-alkenyl complex (**6**).

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