

Kinetic Modeling of the Methanol to Olefins Process. 1. Model Formulation

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Detailed kinetic models at the elementary step level have been formulated for the methanol to olefins (MTO) process over HZSM-5 catalyst with a Si/Al ratio of 200. Starting from plausible mechanisms, the formation of primary products has been modeled rigorously by means of the Hougen–Watson formalism. The formation of higher olefins has been expressed in terms of carbenium ion mechanisms. A computer algorithm has been used to generate the reaction network. The rate coefficient of each elementary step has been formulated according to the single-event approach. The number of single events for each elementary step was calculated from the structure of the activated complex determined by quantum chemical calculations. Activation energies for each elementary step were obtained through the Evans–Polanyi relation that accounts for the various energy levels of carbenium ions and olefin isomers. The single-event kinetics combined with the Evans–Polanyi relation provides a tremendous reduction of the number of parameters to be estimated. Thermodynamic constraints further restrict the number of independent parameters to 33.

Introduction

Light olefins, produced by thermal cracking of ethane, propane, or naphtha, are key components in the petrochemical industry. The zeolite-catalyzed process for the conversion of methanol into olefins provides a promising alternative when cheap natural gas is available. The methanol to olefins (MTO) process originated from Mobil's methanol to gasoline (MTG) process. It is based on a class of synthetic shape-selective zeolites with a high Si/Al ratio.^{1,2} The reduction of the formation of side products is a decisive factor for the commercial application of the process. To achieve this goal, further development of the catalyst and operating conditions, but also detailed mechanistic and kinetic studies, is required.

A review of the MTO process is given by Froment et al.³ Various types of zeolites have been investigated as catalysts for the MTO process, but they greatly suffer from rapid deactivation by coke formation. ZSM-5 and related zeolites are less subject to this type of deactivation. Considerable research has gone into modifications of these catalysts in order to increase the selectivity toward light olefins.^{4–6}

In the present work, a HZSM-5 catalyst with a Si/Al ratio of 200, which was reported as being the most selective among various modified ZSM-5 catalysts, was chosen. Despite considerable research efforts, the mechanism of the initial C–C bond formation, leading to the primary products ethylene and propylene, is not yet completely understood.^{7,8} The formation of higher olefins is known to comprise a large number of reactions.^{9–12} The complexity has led to models in which reactions and

components are strongly lumped.^{13–22} The rate coefficients and adsorption equilibrium constants of such models are not invariant; i.e., they depend on the feed composition and even the type of reactor. In the present work the process is completely written in terms of elementary steps, without any lumping, neither of components nor of steps. The kinetic model is based upon this detailed reaction mechanism. The reaction network describing the formation of C₄–C₈ olefins in terms of elementary steps of carbenium ion chemistry^{9–12} is so large that it has to be generated by the computer algorithm developed by Clymans and Froment.²³ After formulation of rate equations using the Hougen–Watson formalism for each elementary step, the single-event approach is applied to account for the effect of the structure of the reacting species on the change of entropy associated with the elementary step.²⁴ The Evans–Polanyi relation accounts for the effect of structure on the change of enthalpy.²⁵ Quantum chemical calculations are performed to support the application of the approach, which drastically reduces the number of independent parameters. The rate and adsorption parameters obtained in this way are related to the elementary steps, not to lumped reactions, and are truly invariant, regardless of the feed composition and reaction conditions.

Reaction Mechanisms for the MTO Process

The MTO process consists of three categories of reactions: (1) the formation of dimethyl ether (DME), (2) the initial C–C bond formation, and (3) the subsequent conversion of the primary products into higher olefins. Brønsted acidity is known to be the main source of catalyst activity for the formation of the MTO products, while the conjugate Lewis basic site would be responsible for the initial C–C bond formation.

Formation of DME. A reaction scheme for the formation of DME, written in terms of elementary steps, is given in Figure 1 and Table 1. A magic-angle-spinning (MAS) NMR study²⁶ has shown that methanol is revers-

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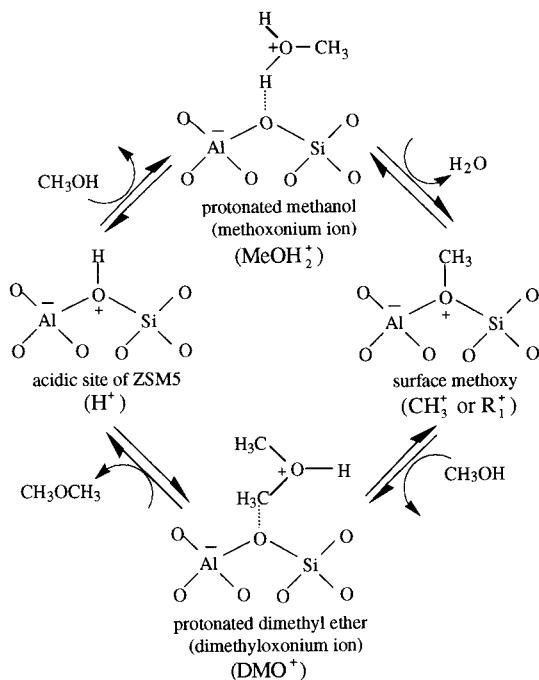


Figure 1. Reaction mechanism for the formation of DME by dehydration of methanol over HZSM-5 catalyst. H⁺ = acidic site of ZSM-5, MeOH₂⁺ = protonated methanol (methoxonium ion), CH₃⁺/R₁⁺ = surface methoxy species, DMO⁺ = protonated DME (dimethyloxonium ion).

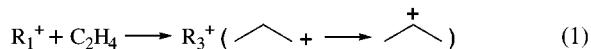
ibly adsorbed through hydrogen to the bridging hydroxyl on the Bronsted sites. The protonation is very fast on strong acidic sites and is considered to reach equilibrium. Quantum chemical calculations using density functional theory by Blaszkowski and van Santen²⁷ revealed that the formation of the adsorbed complex out of methanol or DME does not exhibit an energy barrier. The protonated methanol thus formed leads via dehydration to a surface methoxy species, which is covalently bonded to the lattice oxygen of ZSM-5 and reacts in turn with methanol to form a dimethyloxonium ion (DMO⁺).^{10,11,13,28–30} Deprotonation of the latter yields DME and H⁺. Ono and Mori²⁹ suggested that the methoxy species would release a gas-phase methylcarbenium ion that would be an intermediate in the formation of olefins, but this gas-phase ion is too unstable to play a role and is not considered in the present work.^{10,11}

Formation of Primary Hydrocarbon Products. Among the large number of possible reaction mechanisms for the formation of the initial C–C bond from methanol on acid catalysts, a few mechanisms which are considered to be the most likely have been retained in the present study.^{3,7,31} They are listed in Table 1. The association of the methoxy species (R₁⁺) with a conjugate basic site, bs, leads to three possible pathways based upon a surface-bonded oxonium methylidyl, CH₂, represented by OM (mechanisms a, a', and a''), as suggested by Hutchings et al.³² The association of R₁⁺ with DME leads to a trimethyloxonium (TMO) species, detected in the ¹³C MAS NMR study of Munson and Haw.³³ The possibility of the Stevens rearrangement originally proposed by Van den Berg³⁴ was excluded in this study, given the experimental result on the desilylation with CsF³⁵ of (CH₃)₃SiCH₃O⁺(CD₃)CH₃BF₄⁻.³⁵ Instead, a rearrangement of TMO on a conjugate basic site, yielding a methylene dimethyloxonium ylide (MDOY), as suggested by Forester and Howe²⁸ (viz.,

mechanisms b and b' in Table 1), has been accounted for. The association of R₁⁺ with gas-phase methanol leads to R₂⁺, a carbenium ion with two carbon atoms that decomposes into ethylene (mechanisms d and d'). Hutchings et al.³² suggested this pathway because the basic strength of the ZSM-5 catalyst may not be sufficient to form the oxonium methylidyl by proton abstraction from the methoxy species. Mechanism c, as suggested by Olah et al.,³⁵ involves DMO⁺, whose structure corresponds to protonated DME.

The formation of the methoxy species from the reverse of the steps iii.b/b'.1, iii.b/b'.3, iii.b'.7, and iii.d/d'.1 in Table 1 is not retained because methoxy is too unstable when compared with the other species. The elementary steps involving the surface-associated ylides OM or MDOY shown in iii.a/a''/a''.2, iii.b/b'.3, and iii.c.3 were taken to be irreversible. Ethylene is produced from R₂⁺ in mechanisms a, a', a'', d, and d'. In a and a', R₂⁺ is formed out of OM and protonated methanol and in a'' from OM and DMO⁺. In b, b', and c, ethylene is generated from the ethyldimethyloxonium ion (ED-MO⁺).

A source of propylene is the reaction of methoxy with gas-phase ethylene.³⁸



Deprotonation of the secondary propylcarbenium ion (---^+) yields propylene. The elementary step (1) contains the formation of a highly unstable primary carbenium ion (---^+) but is retained in the reaction network, because the primary propylcarbenium ion is more stable than the methoxy ion. Propylene is also generated by deprotonation of R₃⁺ formed from OM and DMO⁺ as in a and a'', from the decomposition of propyldimethyloxonium ion (PDMO⁺) resulting from the interaction of R₁⁺ with ethylene dimethyloxonium ylide (EDOY) included in mechanism b'²⁸ or from the reaction of methoxy and DME, as in d'. The reaction of methoxy species with gas-phase DME to form ethoxy species was not retained because it requires C–H bond scission in the methyl group of DME, which is highly unlikely.

Methane is also a primary product. In the present study the formation of CH₄ involves the donation of methanol to the surface methoxy,⁷ a step which is supported by the results of experiments with a cofeed of methanol and cycloheptatriene. Because methane is not reactive under MTO conditions, step ii.1 of Table 1 was taken to be irreversible.

Formation of C₄₊ Olefins through Carbenium Ion Chemistry. The formation of higher olefins can be explained by the following elementary steps of carbenium ion chemistry: (1) protonation/deprotonation, (2) hydride, methyl-shift/protonated cyclopropane (PCP)-branching isomerization, (3) methylation/oligomerization, and (4) β scission. Carbenium ions are formed by protonation, which is the interaction of a gas-phase olefin with a Brønsted acid site. Deprotonation is the reverse step. Hydride shift, methyl shift, and PCP branching lead to isomers of carbenium ions and olefins. Under MTO reaction conditions, they reach equilibrium. Methylation and oligomerization increase the chain length of the carbenium ion. They proceed through the reaction between a gas-phase olefin and a surface-

Table 1. Elementary Steps Describing the Formation of Primary Products of the MTO Process and Related Rate and Equilibrium Parameters.

DME Formation				
MeOH + H ⁺	⇒	MeOH ₂ ⁺	$K_{Pr}(\text{MeOH})$	i.1
MeOH ₂ ⁺	⇒	R ₁ ⁺ + H ₂ O	$K_F(R_1^+), K_C(R_1^+)$	i.2
R ₁ ⁺ + MeOH	⇒	DMO ⁺	$K_F(\text{DMO}^+), K_C(\text{DMO}^+)$	i.3
DMO ⁺	⇒	DME + H ⁺	{ $K_{Pr}(\text{DME})$ } ⁻¹	i.4
Methane Formation				
R ₁ ⁺ + MeOH	→	CH ₄ + HCHO + H ⁺	$K_F(\text{CH}_4)$	ii.1
Primary Olefins Formation				
Mechanism a				
R ₁ ⁺ + bs	⇒	OM + H ⁺	$K_{sr}(R_1^+; \text{bs}), K_{sr}(\text{OM}; \text{H}^+)$	iii.a.1
OM + MeOH ₂ ⁺	→	R ₂ ⁺ + H ₂ O + bs	$K_{sr}(\text{OM}; \text{MeOH}_2^+)$	iii.a.2
R ₂ ⁺	⇒	O ₂ + H ⁺	$K_{De}(R_2^+), K_{Pr}(O_2)$	iii.a.3
Mechanism a'				
R ₁ ⁺ + bs	⇒	OM + H ⁺	$K_{sr}(R_1^+; \text{bs}), K_{sr}(\text{OM}; \text{H}^+)$	iii.a'.1
OM + MeOH ₂ ⁺	→	R ₂ ⁺ + H ₂ O + bs	$K_{sr}(\text{OM}; \text{MeOH}_2^+)$	iii.a'.2
R ₂ ⁺	⇒	O ₂ + H ⁺	$K_{De}(R_2^+), K_{Pr}(O_2)$	iii.a'.3
OM + DMO ⁺	→	R ₃ ⁺ + H ₂ O + bs	$K_{sr}(\text{OM}; \text{DMO}^+)$	iii.a'.4
Mechanism a''				
R ₁ ⁺ + bs	⇒	OM + H ⁺	$K_{sr}(R_1^+; \text{bs}), K_{sr}(\text{OM}; \text{H}^+)$	iii.a''.1
OM + DMO ⁺	→	R ₂ ⁺ + MeOH + bs	$K_{sr}(\text{OM}; \text{DMO}^+; R_2^+)$	iii.a''.2
R ₁ ⁺	⇒	O ₂ + H ⁺	$K_{De}(R_2^+), K_{Pr}(O_2)$	iii.a''.3
OM + DMO ⁺	→	R ₃ ⁺ + H ₂ O + bs	$K_{sr}(\text{OM}; \text{DMO}^+; R_3^+)$	iii.a''.4
Mechanism b				
R ₁ ⁺ + DME	→	TMO ⁺	$K_F(\text{TMO}^+)$	iii.b.1
TMO ⁺ + bs	⇒	MDOY + H ⁺	$K_{sr}(\text{TMO}^+; \text{bs}), K_{sr}(\text{MDOY}; \text{H}^+)$	iii.b.2
MDOY + R ₁ ⁺	→	EDMO ⁺ + bs	$K_{sr}(\text{MDOY}; R_1^+)$	iii.b.3
EDMO ⁺	→	O ₂ + DMO ⁺	$K_F(O_2)$	iii.b.4
O ₂ + H ⁺	⇒	R ₂ ⁺	$K_{Pr}(O_2), K_{De}(R_2^+)$	iii.b.5
Mechanism b'				
R ₁ ⁺ + DME	→	TMO ⁺	$K_F(\text{TMO}^+)$	iii.b'.1
TMO ⁺ + bs	⇒	MDOY + H ⁺	$K_{sr}(\text{TMO}^+; \text{bs}), K_{sr}(\text{MDOY}; \text{H}^+)$	iii.b'.2
MDOY + R ₁ ⁺	→	EDMO ⁺ + bs	$K_{sr}(\text{MDOY}; R_1^+)$	iii.b'.3
EDMO ⁺	→	O ₂ + DMO ⁺	$K_F(O_2)$	iii.b'.4
O ₂ + H ⁺	⇒	R ₂ ⁺	$K_{Pr}(O_2), K_{De}(R_2^+)$	iii.b'.5
EDMO ⁺ + bs	⇒	EDOY + H ⁺	$K_{sr}(\text{EDMO}^+; \text{bs}), K_{sr}(\text{EDOY}; \text{H}^+)$	iii.b'.6
EDOY + R ₁ ⁺	→	PDMO ⁺ + bs	$K_s(\text{EDOY}; R_1^+)$	iii.b'.7
PDMO ⁺	→	O ₃ + DMO ⁺	$K_F(O_3)$	iii.b'.8
Mechanism c				
DMO ⁺ + DME	→	TMO ⁺ + MeOH	$K_F(\text{TMO}^+)$	iii.c.1
TMO ⁺ + bs	⇒	MDOY + H ⁺	$K_{sr}(\text{TMO}^+; \text{bs}), K_{sr}(\text{MDOY}; \text{H}^+)$	iii.c.2
MDOY + DMO ⁺	→	EDMO ⁺ + MeOH + bs	$K_{sr}(\text{MDOY}; \text{DMO}^+)$	iii.c.3
EDMO ⁺	→	O ₂ + DMO ⁺	$K_F(O_2)$	iii.c.4
O ₂ + H ⁺	⇒	R ₂ ⁺	$K_{Pr}(O_2), K_{De}(R_2^+)$	iii.c.5
Mechanism d				
R ₁ ⁺ + MeOH	→	R ₂ ⁺ + H ₂ O	$K_F(R_2^+)$	iii.d.1
R ₂ ⁺	⇒	O ₂ + DMO ⁺	$K_{De}(R_2^+), K_{Pr}(O_2)$	iii.d.2
Mechanism d'				
R ₁ ⁺ + MeOH	→	R ₂ ⁺ + H ₂ O	$K_F(R_2^+)$	iii.d'.1
R ₂ ⁺	⇒	O ₂ + H ⁺	$K_{De}(R_2^+), K_{Pr}(O_2)$	iii.d'.2
R ₁ ⁺ + DME	→	R ₃ ⁺ + H ₂ O	$K_F(R_3^+)$	iii.d'.3

associated carbenium ion. The chain length of the carbenium ions is reduced by cracking via the endothermic β scission, which is the reverse of oligomerization. Reaction networks containing the steps mentioned above are also encountered in the work on single-event kinetics of Froment et al.^{24,38–41}

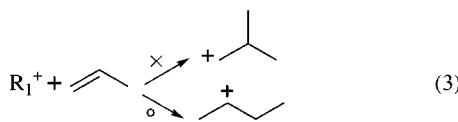
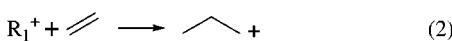
Because of the overwhelming number of elementary steps, the complete MTO reaction network was generated by means of the computer algorithm of Clymans and Froment,²³ further developed, and applied by Baltanas et al.^{24,38–41}

Gas-phase methanol may also be considered as a C₁ species responsible for olefin formation. The sequential addition of gas-phase methanol as a source for chain propagation has been proposed by Sulikowski and

Klinowski, i.e., $\text{CH}_3\text{OH} + R_n^+ \rightarrow R_{n+1}^+ + \text{H}_2\text{O}$ followed by $R_{n+1}^+ \rightarrow C_{n+1}\text{H}_{2n+2} + \text{H}^+$, with $n = 1$ and 2.³⁶ Under MTO conditions, this mechanism is unlikely for the production of C₄₊ olefins because it would lead to a production of ethylene exceeding that of propylene, which is not observed.³⁸ Because there is no positive contribution of entropy, the stability differences between reactant and product cations is the major driving force for the reaction. In the schemes discussed so far, methylcarbenium and primary carbenium ions were excluded because of their instability. In the case of methylation and oligomerization, however, methylcarbenium and some primary carbenium ions have to be considered because of the presence of methoxy and ethoxy species. The methoxy species is formed from the

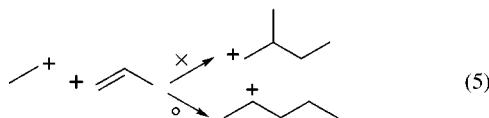
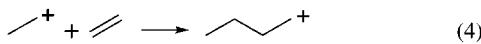
methoxonium ion (protonated methanol). The ethoxy species is also formed, at least partially, from the methoxonium ion and partially also by the protonation of ethylene. Because primary carbenium ions are far less stable than other types of carbenium ions, further formation of higher primary carbenium ions from the reaction of methoxy or ethoxy species with olefins has been retained only when the reactant carbenium ion is less stable than the produced primary ion. The formation of primary ions was not considered when an alternative pathway involving secondary or tertiary carbenium ions is possible.

In the generation of elementary methylation steps, the possibility of the conversion of methoxy into primary carbenium ions depends on the structure of the reacting olefin. Consider the following elementary steps:



Reactions of ethylene and carbenium ions are unlikely because they yield primary cations. When the methylcarbenium ion, R_1^+ , acts as a reactant, however, the elementary step becomes possible, even when a primary cation is formed, because the latter is more stable than the reactant cation. The elementary step (2) represents this particular case. If the methoxy species reacts with propylene, two carbenium products are possible, as shown in (3). In this case, the formation is excluded from the reaction network because the product cation is far more stable than the primary cation. The other types of methylation steps, i.e., methyl into secondary and tertiary ions, are included in the network. Conversely, because the surface-associated methylcarbenium ion is far less stable than a primary cation, the conversion of a primary cation reactant into a methyl cation is not retained.

The elementary steps involving the surface ethylcarbenium ion have been dealt with in a similar way. Oligomerization of a primary into another primary cation is included, but again it depends on the structure of the reactant olefin. The following examples illustrate the similarity with those given in (2) and (3).

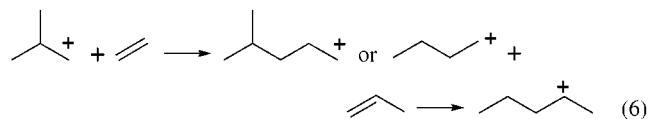


Because the product carbenium ion is more stable than the reactant ion, the elementary step (4) was retained. In (5), however, the formation of 2-methyl-1-butylcarbenium ion, which is primary, is not possible because a preferred route to the 2-pentyl product carbenium ion is available. Again, because of differences between reactant and product carbenium ions, the formation of methyl and primary cations from the reaction of olefins with secondary or tertiary cations has been discarded. Even if some primary carbenium ions can be formed by certain elementary steps, further reactions of those ions

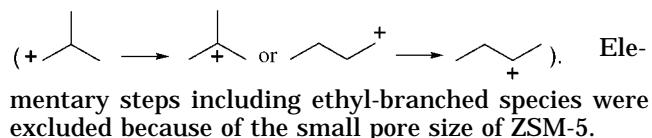
Table 2. Rules for Generating Methylation and Oligomerization Elementary Steps Including Methylcarbenium and Primary Carbenium Ions.

$R^+ + O \rightarrow$	R^+	status
Methylation		
m	p	olefin structure dependent
m	s	allowed
m	t	allowed
Oligomerization		
p	m	not allowed
p	p	olefin structure dependent
p	s	allowed
p	t	allowed
s	m	not allowed
s	p	not allowed
s	s	allowed
s	t	allowed
t	m	not allowed
t	p	not allowed
t	s	allowed
t	t	allowed

with olefins such as



will not occur because of a rapid rearrangement of such carbenium ions into more stable ions



Elementary steps including ethyl-branched species were excluded because of the small pore size of ZSM-5.

Elementary steps consisting of the transformation of a secondary ion into another secondary ion or a secondary ion into a tertiary ion or a tertiary ion into another tertiary ion were evidently accounted for in the oligomerizations. The rules for the generation of methylation and oligomerization are summarized in Table 2. The elementary steps themselves are listed in Tables 3 and 4, while the elementary β scissions are given in Table 5. They are essentially the reverse steps of oligomerization. The formation of methoxy and other primary carbenium ions by β scission is unlikely, because of their unstable nature, so that only secondary and tertiary ions are formed by the cracking steps.

As can be seen in Tables 3–5, the elementary steps are sorted into six categories, depending upon the number of carbon atoms of reactants and products. The types and number of elementary steps generated by the computer algorithm and the species involved in the reaction network are listed in Table 6. Except for ethylene protonation into an ethyl primary carbenium ion, the elementary steps of protonation, deprotonation, and various rearrangements reach equilibrium, so that they are not listed there. Even if the rate coefficients of these steps do not directly appear in the kinetic model, it is important to account for these steps because the surface concentrations of the carbenium ions also depend on them.

Rate Equations

Rate Equations for the Formation of Primary Products. The elementary steps involved in the formation of the primary products are listed in Table 1. The rate of methane formation follows from the elementary

Table 3. List of Elementary Steps of Methylation

Category	(i)	Reaction	Rxn. Index(j)	
$R_1^+ + O_2 \rightarrow R_3^+$	(1)	$R_1^+ + \text{---} \rightarrow \text{---}^+$	(1)	$R_1^+ + \text{---} \xrightarrow{\text{trans}} \text{---}^+$
$R_1^+ + O_3 \rightarrow R_4^+$	(2)	$R_1^+ + \text{---} \rightarrow \text{---}^+$	(1)	$R_1^+ + \text{---} \xrightarrow{\text{cis}} \text{---}^+$
$R_1^+ + O_4 \rightarrow R_5^+$	(3)	$R_1^+ + \text{---} \rightarrow \text{---}^+$	(1)	$R_1^+ + \text{---} \xrightarrow{\text{trans}} \text{---}^+$
$R_1^+ + O_5 \rightarrow R_6^+$	(4)	$R_1^+ + \text{---} \rightarrow \text{---}^+$	(1)	$R_1^+ + \text{---} \xrightarrow{\text{cis}} \text{---}^+$
$R_1^+ + O_6 \rightarrow R_7^+$	(5)	$R_1^+ + \text{---} \rightarrow \text{---}^+$	(1)	$R_1^+ + \text{---} \xrightarrow{\text{trans}} \text{---}^+$
$R_1^+ + O_7 \rightarrow R_8^+$	(6)	$R_1^+ + \text{---} \rightarrow \text{---}^+$	(1)	$R_1^+ + \text{---} \xrightarrow{\text{cis}} \text{---}^+$
		$R_1^+ + \text{---} \rightarrow \text{---}^+$	(2)	

step ii.1 and can be written as

$$R_{\text{CH}_4} = k_F'(\text{CH}_4) C_{R_1^+} P_{\text{MeOH}} \quad (7)$$

The elementary steps entering in the net rate of

formation of DME depend on the mechanisms listed in Table 1. Mechanism a'' will be dealt with here by way of example. The steps to be considered are not only i.3 and i.4 but also iii.a''.2 and iii.a''.3, which generate the ethyl- and propylcarbenium ions, R_2^+ and R_3^+ . Because

Table 4. List of Elementary Steps of Oligomerization

Category	(i)	Reaction	Rxn. Index(j)	$R_3^+ + O_3 \rightarrow R_6^+$ (6)		
		$R_2^+ + O_2 \rightarrow R_4^+$ (1)				(1)
			(1)			(1)
			(1)			(1)
			(1)			(1)
			(1)			(1)
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			(1)			(1)
		<img alt="Chemical reaction diagram showing R3+ reacting with O3 to form R6+. The reactant is R3+ (propyl cation) and the reagent is O3 (ozone). The product is R6				

the deprotonation and protonation involved in i.4 are very fast, DME and DMO^+ are in pseudoequilibrium, so that the net rate of formation of DME can be written as

$$R_{\text{DME}} = r(\text{DMO}^+) = k_{\text{F'}}(\text{DMO}^+) C_{\text{R}_1^+} p_{\text{MeOH}} - \\ k_{\text{C'}}(\text{DMO}^+) C_{\text{DMO}^+} - k_{\text{sr'}}(\text{OM}; \text{DMO}^+ : \text{R}_2^+) C_{\text{OM}} C_{\text{DMO}^+} - \\ k_{\text{sr'}}(\text{OM}; \text{DMO}^+ : \text{R}_3^+) C_{\text{OM}} C_{\text{DMO}^+} \quad (8)$$

Ethylene (O_2) is formed in the equilibrium step iii.a".3 but converted in the first step of the first methylation (Table 3) and oligomerization (Table 4), so that its net

rate of formation is written as

$$R_{O_2} = k_{De}'(R_2^+) C_{R_2^+} - k_{Pr}'(O_2) p_{O_2} C_{H^+} - r_{Me}(1,1) - r_{Ol}(1,1) \quad (9)$$

In the setup of the net rate of formation of propylene (O_3), it has to be accounted for that R_3^+ and O_3 are in pseudoequilibrium, so that

$$R_{O_3} = r(R_3^+) + r(O_3) \quad (10)$$

R_3^+ and O_3 are also involved in various methylations,

Table 5. List of Elementary Steps of β Scission

Category	(i)	Reaction	Rxn. Index(j)
	$R_6^+ \rightarrow O_3 + R_3^+(1)$		(1)
	$R_7^+ \rightarrow O_4 + R_3^+(2)$		(1)
			(2)
			(3)
	$R_8^+ \rightarrow O_5 + R_3^+(3)$		(1)
			(2)
			(3)
			(4)
			(5)
			(6)
			(7)
	$R_7^+ \rightarrow O_3 + R_4^+(4)$		(1)
			(2)
	$R_8^+ \rightarrow O_4 + R_4^+(5)$		(1)
			(2)
			(3)
			(4)
			(5)
			(6)
			(7)
	$R_8^+ \rightarrow O_3 + R_5^+(6)$		(1)
			(2)
			(3)

oligomerizations, and β scissions, so that

$$\begin{aligned}
R_{O_3} = & r_{Me}(1,1) + \sum_{i=1}^3 \sum_j r_{Cr}(i,j) + r_{Cr}(1,1) + \sum_j r_{Cr}(4,j) + \\
& \sum_j r_{Cr}(6,j) - \sum_{i=6}^8 \sum_j r_{Ol}(i,j) - r_{Me}(2,1) - r_{Ol}(2,1) - \\
& r_{Me}(6,1) - \sum_j r_{Ol}(9,j) - \sum_j r_{Ol}(11,j) + \\
& k_{sr}'(OM;DMO^+) C_{OM} C_{DMO^+} \quad (11)
\end{aligned}$$

The rate equations presented above contain the inaccessible concentrations of OM, DMO⁺, R₁⁺, R₂⁺, and R₃⁺

Table 6. Number of Elementary Steps and Species Involved in the Reaction Network for the Formation of C₄₊ Olefins

Number of Species	
olefins	142
carbenium ions	83
total	225
Number of Elementary Steps	
protonation	142
deprotonation	142
hydride shift	88
methyl shift	42
PCP branching	151
methylation	88
oligomerization	52
β scission	21
total	726

ions. These are eliminated in favor of gas-phase concentrations or partial pressures through pseudoequilibrium relationships for steps in which they are involved or, when there is no such step, through the pseudo-steady-state approximation.

Among the elementary steps i.1–i.4, the protonation of MeOH and DME has reached pseudoequilibrium, so that

$$C_{MeOH^+} = K_{Pr}(MeOH) p_{MeOH} C_{H^+} \quad (12)$$

$$C_{DMO^+} = K_{Pr}(DME) p_{DME} C_{H^+} \quad (13)$$

Introducing these relationships into a pseudo-steady-state balance for the concentration of R₁⁺ leads to

$$C_{R_1^+} = \eta_{R_1^+}' C_{H^+} \quad (14)$$

where

$$\eta_{R_1^+}' = \frac{N_{R_1^+}' + k_{sr}'(OM;H^+) C_{OM}}{D_{R_1^+}' + k_{sr}'(R_1^+;bs) C_{bs}}$$

$$\begin{aligned}
N_{R_1^+}' = & k_F'(R_1^+) K_{Pr}(MeOH) p_{MeOH} + \\
& k_C'(DMO^+) K_{Pr}(DME) p_{DME} \\
D_{R_1^+}' = & k_C'(R_1^+) p_{H_2O} + [k_F'(DMO^+) + \\
& k_F'(CH_4)] p_{MeOH} + \sum_i \sum_j k_{Me}'(i,j) p_{O_{kl}} \quad (15)
\end{aligned}$$

In a similar way the concentration of OM ions can be calculated from a pseudo-steady-state balance accounting for all of the elementary steps iii.a".1–3 in which OM is formed and converted:

$$\begin{aligned}
C_{OM} = & \frac{k_{sr}'(R_1^+;bs) \eta_{R_1^+}' C_{bs}}{k_{sr}'(OM;H^+) + (k_{sr}'(OM;DMO^+;R_2^+) + k_{sr}'(OM;DMO^+;R_3^+)) \cdot K_{Pr}(DME) p_{DME}} \quad (16)
\end{aligned}$$

C_{R₂⁺} is obtained from

$$C_{R_2^+} = \eta_{R_2^+}' C_{H^+} \quad (17)$$

with

$$\eta_{R_2^+}' = \frac{k_{sr}'(OM; DMO^+: R_2^+) K_{Pr}(DME) p_{DME} C_{OM} + k_{Pr}'(O_2) p_{O_2}}{k_{de}'(R_2^+) + \sum_{i=1}^5 \sum_j k_{ol}'(i,j) p_{O_{kl}}} \quad (18)$$

Equation 17 is valid also for the calculation of $C_{R_3^+}$, whereas $C_{R_4^+}$ is obtained from

$$C_{R_4^+} = K_{Pr}(O_{ij}) p_{O_{ij}} C_{H^+}, \quad i = 3, 4, \dots, 8 \quad (19)$$

where $O_{ij} + H^+ \rightleftharpoons R_{ij}^+$.

The above equations still contain C_{H^+} and C_{bs} , the concentrations of vacant acid and basic sites. The total concentration of Brønsted acid sites, $C_{H^+}^t$, consists of the vacant plus occupied sites:

$$C_{H^+}^t = C_{H^+} + \sum_i C_{ox} + \sum_j C_{R_{ij}^+} \quad (20)$$

where C_{ox} represents the concentrations of the various surface oxonium ions, such as $MeOH_2^+$, DMO^+ , and TMO^+ . The number of these oxonium ions depends on the reaction mechanisms for the formation of primary products. Still for mechanism a'

$$C_{H^+} = C_{H^+}^t / ads \quad (21)$$

with

$$ads = 1 + K_{Pr}(MeOH) p_{MeOH} + K_{Pr}(DME) p_{DME} + \eta_{R_1^+} + \eta_{R_2^+} + \sum_{i=3}^5 \sum_j K_{Pr}(O_{ij}) p_{O_{ij}}$$

Similarly, the total concentration of the conjugate Lewis basic pair sites, C_{bs}^t , is the sum of the concentration of vacant sites and of those occupied by the various ylide species, C_{yl}

$$C_{bs}^t = C_{bs} + \sum C_{yl} \quad (22)$$

The nature and number of ylides on the catalyst surface again depends on the initial reaction mechanism of the MTO process. Substituting in those equations the concentrations of OM, R^+ , and ylides and solving through symbolic calculations programmed in the code "Mathematica" lead to

$$C_{bs} = \frac{D_{OM} C_{bs}^t}{D_{OM} + k_{sr}(R_1^+; bs) \eta_{R_1^+}} \quad (23)$$

where

$$D_{OM} = k_{sr}(OM; H^+) + [k_{sr}(OM; DMO^+: R_2^+) + k_{sr}(OM; DMO^+: R_3^+)] K_{Pr}(DME) p_{DME}$$

$$\eta_{R_1^+} = (2A_1)^{-1}(-A_2 + \sqrt{(A_2)^2 + 4A_1 A_3})$$

$$A_1 = D_{R_1^+} k_{sr}(R_1^+; bs)$$

$$A_2 = D_{R_1^+} D_{OM} + k_{sr}(R_1^+; bs) [D_{OM} - N_{R_1^+} - k_{sr}(OM; H^+)]$$

$$\begin{aligned} A_3 &= N_{R_1^+} D_{OM} \\ N_{R_1^+} &= k_F(R_1^+) K_{Pr}(MeOH) p_{MeOH} + k_C(DMO^+) K_{Pr}(DME) p_{DME} \\ D_{R_1^+} &= k_C(R_1^+) p_{H_2O} + [k_F(DMO^+) + k_F(CH_4)] p_{MeOH} + \sum_i \sum_j k_{Me}(i,j) p_{O_{kl}} \end{aligned}$$

In eq 23 the total concentrations $C_{H^+}^t$ and C_{bs}^t are incorporated into the rate coefficients, which thereby lose their prime superscript.

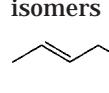
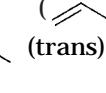
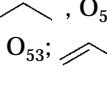
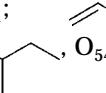
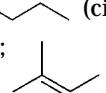
$$k_i(j) = \begin{cases} k'_j C_{H^+}^t C_{bs}^t & i = sr \\ k'_j C_{H^+}^t & i \neq sr \end{cases}$$

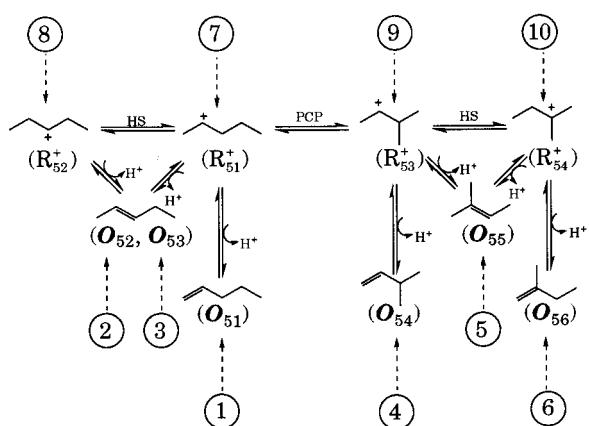
When a rate coefficient is related to a surface elementary step between an acid and a basic site, both $C_{H^+}^t$ and C_{bs}^t are inserted. Only $C_{H^+}^t$ enters into the rate coefficients of the other steps. The rate coefficient, $k_{sr}(TMO^+; bs)$, e.g., is defined as $k_{sr}(TMO^+; bs) = k_{sr}'(TMO^+; bs) C_{H^+}^t C_{bs}^t$, while $k_F(TMO^+)$ is given by $k_F(TMO^+) = k_F'(TMO^+) C_{H^+}^t$.

Rate Equations for the Formation of Higher Olefins. Higher olefins are formed starting from ethylene and propylene by methylation, oligomerization, and β scission occurring on the acid sites of the catalyst and whose rates can be written as

$$\begin{aligned} r_{Me}(i,j) &= k_{Me}'(i,j) C_{R_1^+} p_{O_{kl}} \\ r_{ol}(i,j) &= k_{ol}'(i,j) C_{R_{mn}^+} p_{O_{kl}} \\ r_{Cr}(i,j) &= k_{Cr}'(i,j) C_{R_{mn}^+} p_{O_{kl}} \end{aligned} \quad (24)$$

where i represents the category (viz., Tables 3–5) and j the elementary step in that category. An olefin isomer is represented by O_{kl} , where k is the number of carbon atoms in the olefin. In the present work it lies between 2 and 8. The l is the isomer index within the carbon number. Similarly, a carbenium ion isomer is represented by R_{mn}^+ , where m is the carbon number of the ion, comprised between 1 and 8, and n is the isomer index within the carbon number. The formulation of the net rate of formation of an olefin isomer involves rather large networks and leads to complicated equations. Deprotonation of carbenium ions to produce the corresponding olefins are in pseudoequilibrium, while each olefin isomer participates in other rate-controlling elementary steps such as methylation, oligomerization, and β scission. Consequently, the net reaction rate for each olefin isomer depends not only on the elementary steps containing that olefin isomer but also on the net reaction rate of formation of the corresponding carbenium ion that produces the olefin isomer by deprotonation.

The formulation of the net rate of production of C_5 isomers is taken as an example. There are six olefin isomers (, O_{51} ; , O_{52} ; , O_{53} ; , O_{54} ; , O_{55} ;



- → : Other related rate-controlling elementary steps responsible for the formation of the corresponding olefin or carbenium ion isomer
- ①) $r_{Me}(4,1), r_{Ol}(4,1), r_{Ol}(8,1), r_{Cr}(3,1)$
 - ②) $r_{Me}(4,2), r_{Me}(4,4), r_{Ol}(4,2), r_{Ol}(8,2), r_{Cr}(3,2)$
 - ③) $r_{Me}(4,3), r_{Me}(4,5), r_{Ol}(4,3), r_{Ol}(8,3), r_{Cr}(3,3)$
 - ④) $r_{Me}(4,6), r_{Ol}(4,4), r_{Ol}(8,4), r_{Cr}(3,4)$
 - ⑤) $r_{Me}(4,7), r_{Me}(4,8), r_{Ol}(4,5), r_{Ol}(4,6), r_{Ol}(8,5), r_{Ol}(8,6), r_{Cr}(3,5), r_{Cr}(3,6)$
 - ⑥) $r_{Me}(4,9), r_{Ol}(4,7), r_{Ol}(8,7), r_{Cr}(3,7)$
 - ⑦) $r_{Ol}(2,1), r_{Ol}(11,1), r_{Cr}(6,1)$
 - ⑧) $r_{Me}(3,1)$
 - ⑨) $r_{Me}(3,2), r_{Me}(3,3), r_{Ol}(11,2), r_{Cr}(6,2)$
 - ⑩) $r_{Me}(3,4), r_{Ol}(11,3), r_{Cr}(6,3)$

Figure 2. Reaction network for the formation of C₅ olefin isomers.

, O₅₆) and four carbenium ion isomers (R₅₁⁺; R₅₂⁺; R₅₃⁺, R₅₄⁺) in the C₅ category. Figure 2 shows the reaction network including the isomerization of C₅ carbenium ions, together with the deprotonation of the carbenium ions to produce olefin isomers. Consider the net reaction rate for one of the olefin isomers, O₅₁, formed by the deprotonation of R₅₁⁺. Because the deprotonation is in pseudoequilibrium, the net rate of O₅₁ formation depends on the rate of isomerization of R₅₁⁺, represented by rR_{51}^+ . The olefin isomer O₅₁ is also involved in various other elementary steps, so that the net rate of formation of O₅₁ is given by

$$R_{O_{51}} = r(O_{51}) + r(R_{51}^+) \quad (25)$$

where the elementary steps which determine $r(O_{51})$ and $r(R_{51}^+)$ are given in ① and ⑦ of the caption of Figure 2. The terms in the right-hand side of eq 25 can be written as

$$r(O_{51}) = -r_{Me}(4,1) - r_{Ol}(4,1) - r_{Ol}(8,1) + r_{Cr}(3,1) \quad (26)$$

$$r(R_{51}^+) = r_{Ol}(2,1) - r_{Ol}(11,1) + r_{Cr}(6,1) \quad (27)$$

In the case of O₅₂, the deprotonation of the two carbenium ions R₅₂⁺ and R₅₁⁺ as well as the elementary steps containing O₅₂ is responsible for the rate of formation:

$$R_{O_{52}} = r(O_{52}) + r(R_{51}^+) + r(R_{52}^+) \quad (28)$$

where $r(O_{52})$, $r(R_{51}^+)$, and $r(R_{52}^+)$ can be formulated using ②, ⑦, and ⑧ of the caption of Figure 2. Similarly, the net rate for the other olefins is given by

$$\begin{aligned} R_{O_{53}} &= r(O_{53}) + r(R_{51}^+) + r(R_{52}^+) \\ R_{O_{54}} &= r(O_{54}) + r(R_{53}^+) \\ R_{O_{55}} &= r(O_{55}) + r(R_{53}^+) + r(R_{54}^+) \\ R_{O_{56}} &= r(O_{56}) + r(R_{54}^+) \end{aligned} \quad (29)$$

The distribution of the C₅ olefin isomers can be calculated from their equilibrium composition. The net rate of formation of the olefin lumps (R_{O_5}) is simply the sum of the reaction rates of each olefin isomer

$$R_{O_5} = \sum_j R_{O_{5j}} \quad (30)$$

or more explicitly

$$\begin{aligned} R_{O_5} = & -\sum_j r_{Me}(4,j) - \sum_j r_{Ol}(4,j) - \sum_j r_{Ol}(8,j) + \\ & \sum_j r_{Cr}(3,j) + 2(\sum_j r_{Me}(3,j) + \sum_j r_{Ol}(2,j) - \\ & \sum_j r_{Ol}(11,j) + \sum_j r_{Cr}(6,j)) + \sum_j r_{Ol}(2,j) - r_{Ol}(11,1) + \\ & r_{Cr}(6,1) \end{aligned} \quad (31)$$

In this equation the rates in the right-hand side are given by the equations (24) which contain the carbenium ion concentrations. Again these concentrations are eliminated in favor of the accessible gas-phase species, according to the Hougen-Watson formalism, using elementary steps that are in pseudoequilibrium. The surface concentrations of the C₃₊ carbenium ions are given by

$$C_{R_{ij}^+} = K_{Pr}(O_{ij}) P_{O_{ij}} C_{H^+} \quad (32)$$

When the surface species are not involved in any equilibrated elementary step, the pseudo-steady-state approximation is applied.

To calculate surface concentrations and reaction rates, the values of the rate and equilibrium constants of the elementary steps are required. These are estimated by nonlinear regression from experimental data, as will be developed in detail in part 2 of this work. Each coefficient consists of two parameters: the preexponential factor and the activation energy or heat of adsorption. Table 7 shows the number of parameters required to calculate the rates derived in the previous section. Of the 500 parameters, the majority stems from the network involving carbenium ions. Such a number of parameters cannot be estimated by any reasonable computer algorithm and experimental effort. For the reduction of the number of parameters, the rate coefficients and adsorption equilibrium constants are modeled at a fundamental level as shown in the next section.

Fundamental Modeling of Rate Coefficients and Equilibrium Constants: Single-Event Kinetics

Single-Event Concept. From transition state theory and statistical thermodynamics, Vynckier and Fro-

Table 7. Total Number of Rate Coefficients (k), Equilibrium Constants (K), and Parameters (n_{prm}) in the Reaction Network before Reduction, Using the Single-Event Concept, the Evans-Polanyi Relation, and Thermodynamic Constraints.

Primary Olefins Formation									
	mechanism								
	a	a'	a''	b	b'	c	d	d'	
k	10	11	11	12	16	12	8	9	
K	2	2	2	2	2	2	2	2	
n_{prm}^a	24	26	26	28	36	28	20	22	
Higher Olefins Formation									
k				161					
K				78					
$n_{\text{prm}}^{\text{total}}$				478					
n_{prm}^b	502	504	504	506	514	506	498	500	

^a Number of parameters to be estimated, including temperature dependency. ^b Total number of parameters to be estimated.

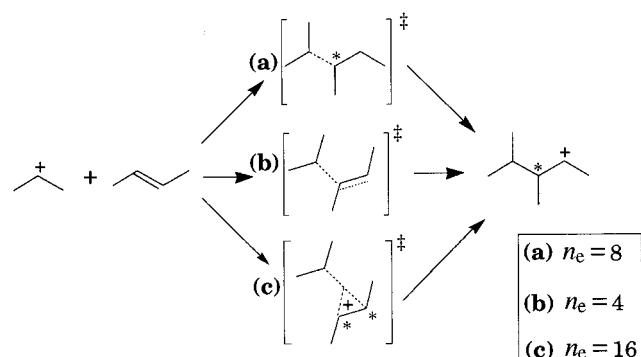


Figure 3. Effect of the configuration of the activated complex on the value of the number of single events.

ment⁴⁰ showed that the rate coefficient of an elementary step, k , is a multiple of the single-event rate coefficient, \tilde{k} :

$$K = n_e \tilde{k} \quad (33)$$

The number of single events, n_e , accounts for the effect of the molecular structure on the entropy contribution to the rate coefficient and is obtained from the ratio of the global symmetry number of the reactant and the transition state.

For intramolecular reactions, the geometry of the activated complex is relatively well defined in the literature. For intermolecular steps, however, particularly for oligomerization or the reverse step, β scission, the structure of the activated complex is not completely clear yet. Figure 3 illustrates how the value of n_e significantly depends on the structure of the activated complex. Three possible structures are considered for the elementary step of oligomerization between the propyl cation and 2-butene, leading to (1) the 2,3-dimethyl-4-pentyl cation, a structure close to that of the product carbenium ion (a in Figure 3), to (2) a structure close to that of the reactants (b in Figure 3), or to (3) a cyclic structure consistent with the activated complex in the methyl shift (c in Figure 3). Depending on the structure of the activated complex, n_e varies from 4 to 16. This difference is due to the contributions of the number of chiral atoms in the activated complex (denoted by asterisks in Figure 3).

The transition state is defined as a configuration containing the highest potential energy in the course of the elementary step. In the present work a semiem-

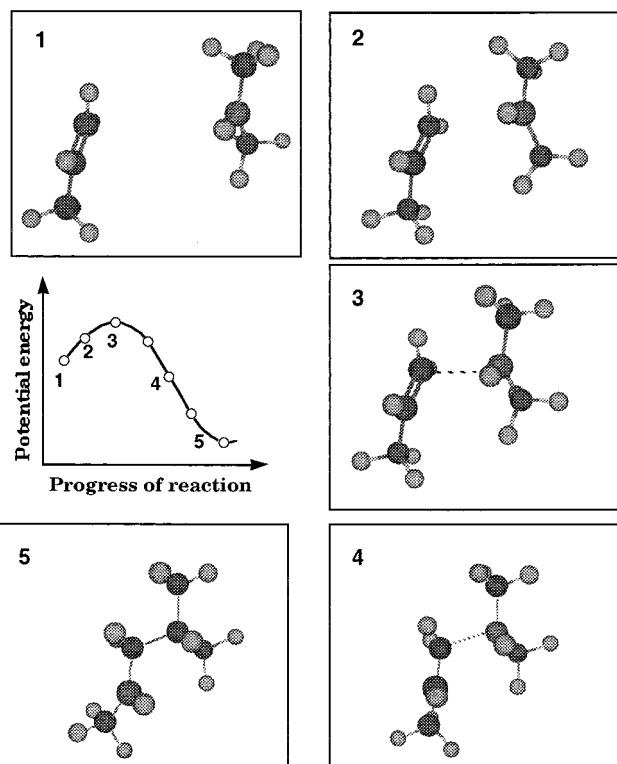


Figure 4. Calculation of the reaction path for the oligomerization between propylene and propylcarbenium ion using MOPAC 93.

pirical quantum chemical calculation was performed, using the general purpose molecular orbital package MOPAC 93.⁴² Oligomerization between a propylcarbenium ion and propylene is taken as an example. To determine the molecular structure of the activated complex, a reaction path calculation was performed, generating each transformation of the elementary step (Figure 4). A total of 18 states was generated in search of the maximum potential energy. Five of these structures are shown in Figure 4. The molecular structure 3, in which the distance between the two reactants is 2.4 Å, was found to have the highest energy. This geometry has been refined by three optimization routines: (1) Bartel's nonlinear least-squares gradient minimization algorithm,⁴³ (2) the McIver-Komornicki gradient norm minimization,⁴⁴ and (3) the eigenvector following routine.⁴⁵ The optimized structures obtained from these three methods were almost identical. They were also very close to the structure shown in Figure 4. It was confirmed through the calculation of the Hessian matrix, which should not contain more than one imaginary vibrational frequency. As a final step of verification of the transition state, the internal reaction coordinate (IRC) calculation successfully generated the reactant and the product starting from the configuration of the activated complex.

All of the structures of the activated complexes for the methylation, the oligomerization, and β scission were determined by the quantum chemical approach described above. The structures of the activated complexes were close to those of the reactants: the double bond of the olefins involved in the elementary step still existed in the transition state. According to the Hammond postulate,⁴⁶ the structure of the transition state is close to that of the reactants when the elementary step is exothermic. The activated complex obtained from

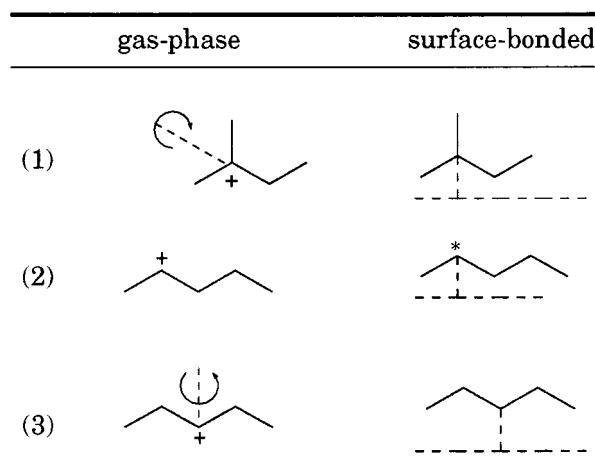


Figure 5. Differences in structure between free and surface-bonded carbenium ions.

the calculations outlined above has been used to calculate the number of single events of the elementary steps.

Number of Single Events. In the calculation of the number of single events, the gas-phase transition states were used. From IR spectroscopic high-resolution ^{13}C MAS NMR and ab initio calculations, Kazansky⁴⁷ concluded that alkylcarbenium ions are rapidly converted into surface alkoxy groups which are covalently bonded to the surface oxygen ions. The global symmetry number of such a configuration is different from that of the gas-phase carbenium ion. The difference mainly comes from the loss of twofold axes for tertiary carbenium ions with more than four carbon atoms, from additional chirality on the positively charged carbon atom of the gas-phase ion, and from the loss of external symmetry. Those effects result in a reduction of the global symmetry number of the surface-associated carbenium ions. Consider as an example the three C_5 ions shown in Figure 5. In the case of structure (1) the twofold axes in the gas-phase carbenium ion are lost upon linking to the catalyst active site. The surface-associated secondary carbenium ion (2) has an additional chiral atom that does not exist in the corresponding gas-phase ion. The sp planar structure of the gas-phase carbenium ion shown in (3) contains external symmetry axes, which is not the case any more when it is linked to an active site of the catalyst. The global symmetry number is reduced by a factor of 2. The global symmetry number for the surface-associated activated complex is also reduced by a factor of 2, so that the number of single events is the same as that obtained from gas-phase structures.

Single-Event Rate Coefficients. To reduce the number of parameters, assumptions had to be introduced. It was assumed that within a given class of elementary steps the single-event rate coefficient, \tilde{k} , only depends on the type of carbenium ions (secondary and tertiary).²⁴ Because of the presence of methoxy and primary carbenium ions in the reaction network, the reduction is rather limited in the MTO process. In addition, an inspection of the experimental heats of formation of gas-phase carbenium ions revealed that even within one and the same type of carbenium ion the energy level still varies with its structure.

In the present work \tilde{k} is expressed according to the Arrhenius relation:

$$\tilde{k} = \tilde{A} \exp(-E/RT) \quad (34)$$

Table 8. Single-Event Preexponential Factors for Deprotonation of 2-Butylcarbenium Ion

elementary steps	A'	n_e	\tilde{A}
$\text{---} + \text{H}^+ \rightarrow \text{---} + \text{H}_2\text{O}$	$2.658 \cdot 10^{15}$	3	$8.860 \cdot 10^{14}$
$\text{---} + \text{H}^+ \rightarrow \text{---} + \text{H}_2\text{O}$	$8.859 \cdot 10^{14}$	1	$8.859 \cdot 10^{14}$

\tilde{A} depends on the molecular structure, because it is linked to the elementary step through the change of entropy. Attempts were made to validate the single-event preexponential factor by data on the elementary steps gas-phase carbenium ion transformations obtained by Dumesic et al.³⁷ The deprotonation of 2-butyl cation was taken as an example (Table 8). Dividing A' (in molecules per second) by n_e yields the single-event preexponential factor, \tilde{A} . The value of A calculated in this way is almost identical to the value obtained in the present work. The activation energy is calculated from the Evans–Polanyi relation, to be discussed in the following section.

Application of the Evans–Polanyi Relation. To account for the effect of energy level differences in carbenium ions and olefin isomers on the rate coefficients, the Evans–Polanyi relation, also called linear free energy relation,⁴⁹ was introduced. For exothermic elementary steps of the type i , the activation energy $E_f(j,k)$ for the k th reaction of the category j is given by $E_f(j,k) = E_i^\circ - \alpha_i |\Delta H_i(j,k)|$. The single-event rate coefficient of the elementary step can then be written as

$$\tilde{k}_i(j,k) = \tilde{A}_i \exp\left(-\frac{E_i^\circ - \alpha_i |\Delta H_i(j,k)|}{RT}\right) \quad (35)$$

The activation energy $E_f(j,k)$ for the corresponding reverse endothermic elementary steps of type i' can be written as $E_{i'}^\circ + (1 - \alpha_i) |\Delta H_i(j,k)|$ and eq 35 is adapted.

The intrinsic activation barrier, E_i° , and the transfer coefficient, α_i , only depend on the type of elementary step, so that there are only two parameters which need to be estimated to obtain the activation energy for each elementary step of a given class. Given the thermodynamic relation $\Delta H_i(j,k) = E_i(j,k) - E_f(j,k)$, they are also valid for the reverse steps. The single-event rate coefficients for each elementary step of methylation and oligomerization were calculated by means of eq 35. The same values of E_i° and α_i were used for both methylation and oligomerization, because the nature of the two reactions is essentially the same. For the rate coefficients of the β scission, a thermodynamic relationship has been used instead of the endothermal version of eq 35, because it provides a further reduction of the number of parameters.

Reduction of the Number of Parameters through Thermodynamic Constraints

Relation between the Thermodynamic Properties of Gas-Phase and Surface-Associated Carbenium Ions. The application of the Evans–Polanyi relation requires the numerical values of the heats of reaction. These can only be calculated when the thermodynamic properties of the surface-associated carbenium ions are available. A direct measurement of all of the involved cations is neither reliable nor realistic because of the fast rearrangement and the large number of carbenium ions. Theoretical calculations using semiempirical or ab initio methods including the structure of

ZSM-5 is a task beyond the capability of today's computers. The zeolite structure is presently represented by a simple cluster Si—O—Al—O—Si,²⁷ which cannot reflect the acid strength of the active site with sufficient precision.

Because it is generally accepted that the transformation of carbenium ions in the zeolite can be represented by those of the ion in the gas phase,^{8–11} the thermodynamic properties of the surface cations have to be related to those of the gas phase. Because of the stabilization effect of the zeolite framework, it is obvious that the surface carbenium ion is more stable. The heat of stabilization $q(R_i^+)$ can be written as

$$q(R_i^+) = \Delta H_{f,g}^\circ(R_i^+) - \Delta H_{f,s}^\circ(R_i^+) \quad (36)$$

where $\Delta H_{f,g}^\circ(R_i^+)$ and $\Delta H_{f,s}^\circ(R_i^+)$ represent the standard heat of formation of the gas-phase and surface-associated carbenium ions, respectively. The $q(R_i^+)$ is a positive and catalyst-dependent quantity. The higher the acid strength of the catalyst, the larger the value of $q(R_i^+)$. For a given catalyst Dumesic et al.³⁹ considered this heat of stabilization as a constant quantity for all of the carbenium ions of the reaction network. They introduced a catalyst-dependent parameter, ΔH_+ , that is, the heat of stabilization of the proton relative to the carbenium ion in the zeolite framework. The application of this assumption to the MTO process was unsuccessful. It was observed that the amount of formation predicted by the model based upon this approach was significantly lower than the experimental value. One of the main reasons was that the light carbenium ions are too unstable relative to the higher ions, so that their rate of consumption was overestimated. Intuitively, $q(R_i^+)$ should not strongly depend on the structure or type of carbenium ions provided they have the same number of carbon atoms. If it would, the reaction paths of the isomerization of the carbenium ions on the zeolite would be considerably different from those in the gas phase. It seems reasonable that large carbenium ions would have a more delocalized positive charge than smaller ions, so that less additional stabilization is available to them when they are linked to the surface. Among the various other possibilities, it was found in the present work that when the heat of stabilization was assumed to depend on the number of carbon atoms, the MTO experimental data were accurately predicted and that the parameter values satisfied the physicochemical and statistical tests.

Reduction of the Number of Parameters. Although the combination of the single-event concept and the Evans–Polanyi relation led to a significant reduction of the number of rate coefficients from 500 to 200, a large number of adsorption equilibrium constants remain to be estimated to obtain the surface concentrations of the carbenium ions which enter into the kinetic equations. The introduction of thermodynamic constraints into the olefin isomerization network further reduced the number of independent parameters from 75 down to 6.

The isomerization of the C₅ olefins through the corresponding carbenium ions is taken here as an example. Consider the overall equilibrium constant for the isomerization of O₅₁ into O₅₆ involving O₅₁, R₅₁⁺, R₅₃⁺, R₅₄⁺, and O₅₆. The equilibrium constant for the isomerization between those two olefins can be ex-

pressed as the product of the equilibrium constants of the steps occurring in their isomerization

$$K_{\text{Iso}}(\text{O}_{51} \rightleftharpoons \text{O}_{56}) = K_{\text{Pr}}(\text{O}_{51}) K_{\text{PCP}}(\text{R}_{51}^+ \rightleftharpoons \text{R}_{53}^+) K_{\text{HS}}(\text{R}_{53}^+ \rightleftharpoons \text{R}_{54}^+) K_{\text{Pr}}^{-1}(\text{O}_{56}) \quad (37)$$

For an elementary step the equilibrium constant can be expressed as the ratio of the forward and reverse rate coefficients. Using this property, together with the expression for the rate coefficient expliciting the number of single events, the Evans–Polanyi relation for the protonation of O₅₁ can be written as

$$K_{\text{Pr}}(\text{O}_{51}) = K_{\text{Iso}}(\text{O}_{51} \rightleftharpoons \text{O}_{56}) K_{\text{Pr}}(\text{O}_{56}) \left(\frac{\sigma_{\text{gl}}^{\text{R}_{54}^+}}{\sigma_{\text{gl}}^{\text{R}_{51}^+}} \right) \left(\frac{\Delta H_{f,s}(\text{R}_{51}^+) - \Delta H_{f,s}(\text{R}_{54}^+)}{RT} \right) \quad (38)$$

The difference between the heats of formation $\Delta H_{f,s}(\text{R}_{51}^+) - \Delta H_{f,s}(\text{R}_{54}^+)$ is calculated from the properties of the gas-phase carbenium ions, because it is preserved on the catalyst. It can be shown that, regardless of the number of ions involved in the reaction pathway connecting the two olefins, eq 38 holds for any other equilibrium constant with respect to the olefin–carbenium pair O₅₆ and R₅₄⁺ involved in the protonation. The importance of eq 38 becomes clear when it is rewritten as follows:

$$K_{\text{Pr}}(\text{O}_i) = K_{\text{Iso}}(\text{O}_i \rightleftharpoons \text{O}_{i'}) K_{\text{Pr}}(\text{O}_{i'}) \left(\frac{\sigma_{\text{gl}}^{\text{R}_{i'}^+}}{\sigma_{\text{gl}}^{\text{R}_i^+}} \right) \left(\frac{\Delta H_{f,g}(\text{R}_{i'}^+) - \Delta H_{f,g}(\text{R}_i^+)}{RT} \right) \quad (39)$$

O_i and R_{i'}⁺ represent the olefin carbenium ion pair in a reference protonation step, O_i + H⁺ ⇌ R_{i'}⁺, whereas O_i and R_{i'}⁺ are the olefin isomer and the corresponding carbenium ion in the actual protonation step. Equation 39 shows that within a fraction with a given number of carbon atoms any protonation equilibrium constant can be calculated from that of the reference protonation and the thermodynamic properties of the gas-phase carbenium ions. Consequently, at a given temperature there is only one independent protonation equilibrium constant per carbon number. The number of protonation equilibrium constants required to calculate all of the surface concentrations of the carbenium ions is thus reduced from 78 to 6, i.e., one per carbon number (from C₃ to C₈). When the temperature dependence of the equilibrium constants is included, the number of independent parameters for protonation amounts to 12. The equilibrium constant for the C₂ fraction was already defined by $K_{\text{Pr}}(\text{O}_2)$ and $K_{\text{De}}(\text{R}_2^+)$ in the discussion of the rate equations of the initial elementary steps of the MTO network.

The equilibrium constants of all of the reference protonation steps including the C₂ fraction can be parametrized further using the expression for the rate coefficient based upon the number of single events and the single-event preexponential factor. The equilibrium constants for the seven reference protonation steps, O_i + H⁺ ⇌ R_{i'}⁺, can be written as

$$K_{\text{Pr}}(\text{O}_{ii}) = \frac{K'_{\text{Pr}}(\text{O}_{ii})}{K'_{\text{De}}(\text{R}_{ii}^+)} = \left(\frac{\sigma_{\text{gl}}^{\text{O}_{ii}}}{\sigma_{\text{gl}}^{\text{R}_{ii}^+}} \right) \tilde{A}_{\text{Pr}} \exp \left(- \frac{\Delta H_{\text{Pr}}(\text{O}_{ii})}{RT} \right), \\ i = 2, 3, \dots, 8 \quad (40)$$

Because the single-event preexponential factor only depends on the type of elementary step, the ratio of single-event preexponential factors $\tilde{A}_{\text{Pr}}/\tilde{A}_{\text{De}}$ should be the same for the seven carbon number fractions. According to transition state theory, it can also be expressed as the difference in entropy between the reactants and product, i.e., $\tilde{A}_{\text{Pr}}/\tilde{A}_{\text{De}} = \exp(\Delta \tilde{S}_{\text{Pr}}/R)$, so that

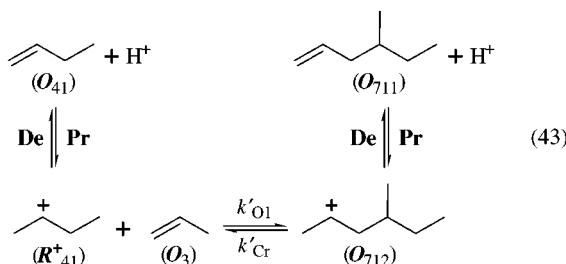
$$K_{\text{Pr}}(\text{O}_{ii}) = \left(\frac{\sigma_{\text{gl}}^{\text{O}_{ii}}}{\sigma_{\text{gl}}^{\text{R}_{ii}^+}} \right) \exp \left(\frac{\Delta \tilde{S}_{\text{Pr}}}{R} \right) \exp \left(- \frac{\Delta H_{\text{Pr}}(\text{O}_{ii})}{RT} \right), \\ i = 2, 3, \dots, 8 \quad (41)$$

Using eq 41, the number of parameters is reduced to six. The deprotonation rate coefficient for the C_2 -fraction, $K'_{\text{De}}(\text{R}_2^+)$ can be calculated from

$$K'_{\text{De}}(\text{R}_2^+) = K_{\text{Pr}}(\text{O}_2)/K_{\text{Pr}}(\text{O}_2) \quad (42)$$

and six preexponential factors for $K_{\text{Pr}}(\text{O}_{ii})$ can be represented by one parameter, $\Delta \tilde{S}_{\text{Pr}}$, because it is independent of the number of C atoms or type of carbenium ion.

The $\Delta H_{\text{Pr}}(\text{O}_{ii})$, where $i = 2, 3, \dots, 8$, will be dealt with as the parameters to be estimated. It can be concluded that only seven parameters out of 156 (78×2) parameters are truly independent. Because β scission is the reverse step of oligomerization, a similar approach based upon thermodynamic relations can be applied to the rate coefficients of β scission. Consider the oligomerization/ β scission (Tables 4 and 5), together with the protonation/deprotonation for the reactant and product carbenium ion:



The overall equilibrium constant for the formation of O_{711} out of O_{41} and O_3 can be expressed as the product of the equilibrium constants of the steps involved in the reaction pathway, i.e., $K_{\text{O}1}(\text{O}_{41} + \text{O}_3 \rightleftharpoons \text{O}_{711}) = K_{\text{Pr}}(\text{O}_{41}) (K_{\text{O}1}/K_{\text{Cr}}) K_{\text{Pr}}^{-1}(\text{O}_{711})$, so that the rate coefficient for the β -scission is given by

$$K_{\text{Cr}} = K_{\text{O}1} K_{\text{Pr}}(\text{O}_{41}) K_{\text{Pr}}^{-1}(\text{O}_{711}) K_{\text{O}1}(\text{O}_{41} + \text{O}_3 \rightleftharpoons \text{O}_{711}) \quad (44)$$

The oligomerization rate coefficient can be calculated from the single-event kinetic approach through eq 35. The protonation equilibrium constant, $K_{\text{Pr}}(\text{O}_{41})$, can be obtained from eq 41, while the overall equilibrium constant is obtained from the thermodynamic properties of the corresponding olefin isomers. Because the reaction network (43) is valid for any elementary step of β scission, the rate coefficients of this elementary step are not independent. In other words, no additional param-

eters are required to predict the rates of β scission. The total number of independent parameters left is on the order of 33, depending on the number of parameters in the primary product network.

Equations 39 and 44 can only be applied when the thermodynamic properties of the gas-phase carbenium ions and olefin isomers are known. For olefins with more than six carbon numbers, a complete set of experimental data for the thermodynamic state function is not available in the literature. In the present study the properties of olefins were estimated by Benson's group contribution method⁵⁰ and those of carbenium ions by quantum chemical calculations. From a comparison with published data, it was concluded that semiempirical methods were not sufficiently accurate to reproduce the trend in relative stability differences between carbenium ions of a given type and with the same number of carbon atoms, which is observed in experimental data. Ab initio calculations of the STO-3G level were required for this purpose.

Conclusion

In this first part the detailed kinetic modeling of the MTO process based upon elementary steps has been carried out, for the formation of both the primary products and the higher olefins. The number of parameters was reduced by the use of the single-event concept, combined with the Evans–Polanyi relation. The number of independent adsorption equilibrium constants was reduced by thermodynamic constraints. The total number of kinetic and adsorption parameters finally amounts to 33. These remain to be determined from experimental data, and this step will be dealt with in part 2.

Notation

- A' = preexponential factor of an elementary step
- A'_i = preexponential factor of an elementary step of type i
- \tilde{A}_i = single-event preexponential factor of reaction type i
- C_{bs}^t = total concentration of basic sites, mol/g_{cat}
- $C_{\text{H}^+}^t$ = total concentration of acid sites, mol/g_{cat}
- C_i = concentration of surface species i , mol/g_{cat}
- E_a^o = intrinsic activation barrier in the Evans–Polanyi relation, J/mol
- E_{act} = activation energy, J/mol
- E_i = activation energy of reaction type i
- h = Plank constant: 1.841×10^{-37} , J·h
- K_i = equilibrium constant of an elementary step i
- $K_i(j)$ = equilibrium constant of an elementary step of type i for species j
- k_B = Boltzmann constant: 1.381×10^{-23} , J/K
- K_i = rate coefficient of an elementary step i
- $K'_i(j)$ = rate coefficient of an elementary step of type i
- $K'_i(j,k)$ = rate coefficient of an elementary step of type i in j th category and k th reaction
- $K'_i(j,k)$ = rate coefficient of an elementary step of type i for the reaction of surface species j with surface species k
- k = rate coefficient multiplied by $C_{\text{H}^+}^t$ and/or C_{bs}^t
- \tilde{k} = single-event rate coefficient
- n_{ch} = number of chiral centers
- n_e = number of single events
- n_{prm} = number of parameters to be estimated
- O_{ij} = olefin with carbon number, i ($i = 2, 3, \dots, 8$), and isomer index, j
- p_i = partial pressure of gas-phase species i , bar
- $q(i)$ = heat of stabilization for species i , J/mol
- R_{ij}^+ = carbenium ion with carbon number, i ($i = 1, 2, \dots, 8$), and isomer index, j

S° = standard entropy, J/mol·K

s = secondary

t = tertiary

R_i = net reaction rate for gas-phase species i , mol/g_{cat}·h

R = gas constant: 8.314, J/mol·K

$r(i)$ = reaction rate for species i , mol/g_{cat}·h

$r_i(j)$ = reaction rate of type i for species j , mol/g_{cat}·h

$r_{i(j,k)}$ = reaction rate of an elementary step of type i at j th category and k th reaction, mol/g_{cat}·h

T = temperature, K

Greek Letters

α = transfer coefficient in the Evans-Polanyi relation

η'_i = ratio of concentration of surface species i to that of acid site

ΔH^\ddagger = standard enthalpy of activation, J/mol

$\Delta H_f^\ddagger(i)$ = standard enthalpy of formation for species i , J/mol

$\Delta H_r(i)$ = heat of reaction of an elementary step i , J/mol

$\Delta H_{r(j,k)}$ = heat of reaction of elementary step of type i in j th category and k th reaction, J/mol

ΔG_i = standard Gibbs' free energy change of reaction type i , J/mol

ΔS^\ddagger = standard entropy of activation, J/mol·K

$\Delta q_+(i)$ = difference in heat of stabilization between proton and species i , J/mol

σ = symmetry number

σ_{gl}^i = global symmetry number of species i

Subscripts

bs = basic site

C = consumption

Cr = cracking

De = deprotonation

ext = external

F = formation, used in the rate coefficient

f = formation, used in the enthalpy

g = gas phase

iso = isomerization

Me = methylation

MS = methyl shift

OI = oligomerization

ox = oxonium ion

Pr = protonation

r = reaction

s = surface

sr = surface reaction

trans = translation

vib = vibration

rot = rotation

sym = symmetry

yl = ylide species

Superscripts

r = reactant

t = total

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