

Metal Ions Control the Competition between β - and γ -Hydrogen Transfer in the Generation of Propene from 1,7-Octadiene in the Gas Phase

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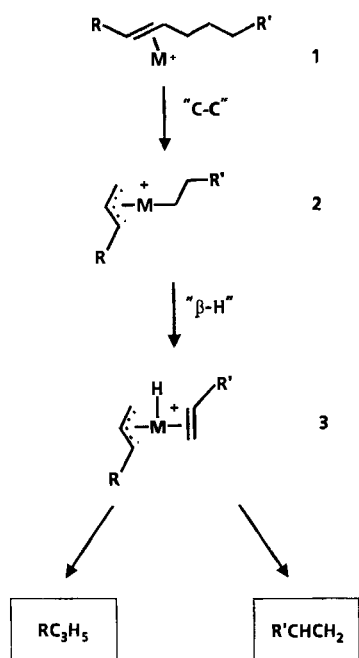
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The mechanistic details (i.e. β - versus γ -hydrogen transfer) of transition-metal ion induced generation of propene from metastable ion complexes of 1,7-octadiene with $M^+ = Cr^+, Fe^+, Ni^+$ are strongly affected by the nature of M^+ . For Cr^+ the major reaction involves the transfer of an allylically activated hydrogen atom to M^+ (γ -H transfer), followed by coupling of

this hydrogen with the C_3H_5 unit (Scheme 3: $8 \rightarrow 9 \rightarrow 11 \rightarrow C_3H_6$). The hydrogen transfer $9 \rightarrow 11$ is preceded by substantial exchange reactions. A minor path for $M^+ = Cr^+$ corresponds to the more traditional β -hydrogen transfer $9 \rightarrow 10$. This process, however, represents the major route for propene loss induced by $M^+ = Fe^+, Ni^+$.

There exists ample experimental evidence for the highly regioselective reactions of bare transition-metal ions M^+ with olefins. The reaction commences with the complexation of the π -bond by the metal ions, followed by oxidative addition of the allylic C—C bond to M^+ (Scheme 1: $1 \rightarrow 2$); the insertion is completed by β -hydrogen transfer to produce a complex **3**, which eventually undergoes reductive elimination of RC_3H_5 or ligand detachment (loss of $RCH=CH_2$), as originally proposed by Beauchamp et al.¹⁾ and later confirmed by Ridge, Gross, and co-workers²⁾. The specificity of the overall reaction (Scheme 1) is such that, by detachment of the less strongly bound ligand, an unambiguous location of the double bond can be achieved.

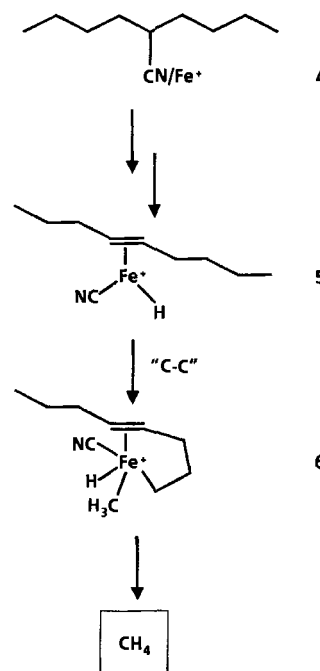
Scheme 1



However, as indicated in Scheme 2, allylic activation needs not necessarily be the dominant mode of C—C or C—H bond acti-

vation of alkenes. For example, detailed studies³⁾ of Fe^+ complexes of α -branched aliphatic nitriles, e.g. **4**, have revealed for the gas-phase generation of CH_4 an unprecedented reaction mechanism, which involved the following steps: (i) insertion of Fe^+ into the C—CN bond and β -hydrogen transfer (Scheme 2: $4 \rightarrow 5$), (ii) oxidation of a *remote*⁴⁾ H_3C —C bond, $5 \rightarrow 6$, and (iii) reductive elimination of CH_4 . In fact, there is increasing evidence⁵⁾ that cooperative effects, exerted by the presence of several functional groups and orchestrated by a transition-metal ion, cause highly selective reactions which are often unknown for the monofunctional systems.

Scheme 2



In this paper we report on the metal-ion ($M^+ = Cr^+, Fe^+, Ni^+$) mediated formation of propene from 1,7-octadiene (**7**) in the gas phase⁶⁾. If the traditional concept, which is operative for simple

alkenes, applies also to the loss of propene from metastable ion⁷⁾ complexes **8**, the neutral is predicted to originate from C-1–C-2–C-3 and one hydrogen atom which is provided by C-5 (Scheme 3: **9**→**10**). Alternatively, the C–C double bond of the C₅ ligand may activate its allylic C–H bond such that a hydrogen atom from this position is transferred to the metal ion (**9**→**11**), followed by re-

Scheme 3

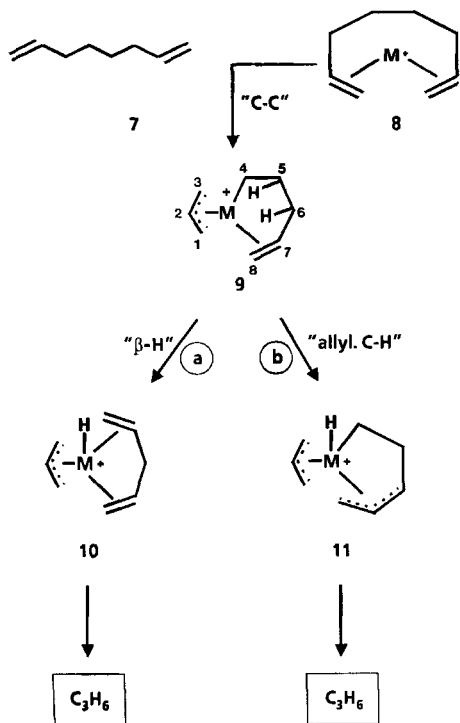


Table 1. Labeling distribution for the M⁺ (M⁺ = Fe⁺, Ni⁺, Cr⁺) mediated formation of propene from 1,7-octadiene isotopomers

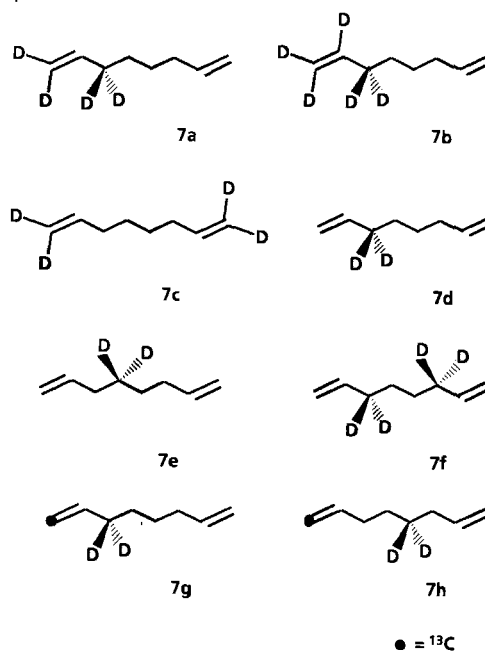
Precursor	M ⁺	Δm					
		42	43	44	45	46	47
7a-M ⁺	Cr ⁺	12	24	9	14	41	
	Fe ⁺	38	11	11	8	32	
	Ni ⁺	33	15	18	14	20	
7b-M ⁺	Cr ⁺	4	30	17	10	21	18
	Fe ⁺	33	7	12	12	8	28
	Ni ⁺	26	13	17	16	10	18
7c-M ⁺	Cr ⁺	—	11	80	9		
	Fe ⁺	2	12	82	4		
	Ni ⁺	3	16	71	10		
7d-M ⁺	Cr ⁺	15	30	55			
	Fe ⁺	45	24	31			
	Ni ⁺	45	30	25			
7e-M ⁺	Cr ⁺	69	26	5			
	Fe ⁺	56	37	7			
	Ni ⁺	62	30	8			
7f-M ⁺	Cr ⁺	—	—	36	64		
	Fe ⁺	2	11	83	4		
	Ni ⁺	3	18	70	9		
7g-M ⁺	Cr ⁺	18	18	11	53		
	Fe ⁺	40	11	13	36		
	Ni ⁺	35	23	19	23		
7h-M ⁺	Cr ⁺	55	25	20	—		
	Fe ⁺	46	22	28	4		
	Ni ⁺	49	21	27	3		

^{a)} Intensities are normalized to ΣΔm = 100% for a given complex.

ductive elimination of C₃H₆. The latter reaction would correspond to a γ-hydrogen transfer which is much less prevalent in organo-metallic systems compared with β-hydrogen transfer.

While a structural characterization of the species generated in the course of C₃H₆ formation from **8** is not yet feasible, the study of the set of D- and ¹³C-labeled 1,7-octadienes **7a–7h** (Scheme 4) reveals some unexpected findings. Most notable is the observation that the Fe⁺ and Ni⁺ complexes give an isotope distribution (Table 1) which is quite different from that observed for the Cr⁺ complexes; in addition, an analysis of the labeled substrates clearly indicated that extensive rearrangements precede the formation of C₃H₆.

Scheme 4



Let us first discuss the Cr⁺-induced formation of C₃H₆ from **7**. From the analysis of the data of **7a, e, h, f** it follows that path (a) accounts for ≥ 60%. Due to unknown isotope effects a more quantitative estimate is not possible. Path (b), the prototypical mechanism for alkene loss, contributes roughly to 25–30% of the total propene formation. Interestingly, path (b) is subject to reversible hydrogen exchange preceding the detachment of propene. This is indicated by, for example, the loss of Δm = 44 (11%) from **7g-Cr⁺**. If paths (a) and (b) were operative without prior hydrogen exchange one should only observe signals corresponding to Δm = 42, 43, and 45, respectively. Similarly, losses of Δm = 44, 45 in the spectrum of **7a-Cr⁺** and of Δm = 43, 45 from **7c-Cr⁺** can only be accounted for by hydrogen exchange reactions. There exist at least two mechanistic variants which, however, cannot yet be distinguished: (i) Process **9**→**11** is reversible and may involve a double-bond shift from the terminal to an internal position. (ii) The C–C bond cleavage **8**→**9** is preceded by a reversible isomerization, e.g. 1,7-octadiene ⇌ 1,6-octadiene ⇌ 2,6-octadiene. An even more complex variant may involve the reversible isomerization 1,7-octadiene ⇌ cyclooctene⁸⁾. Interestingly, for path (a) exchange processes due to a reversibility of the reaction **9**→**10** are much less pronounced. This follows directly from the low intensity (5%) signal corresponding to Δm = 44 in the spectrum of **7e-Ce⁺**.

In view of the results of a recent study⁹⁾ on the specific Fe⁺-induced loss of ethylene from the *internal, intact* CH₂ groups C-4/

C-5 of **7**, we are quite surprised to note from the data listed in Table 1 that propene elimination from **7-Fe**⁺ is much less specific. Surprisingly, the reactions with **Fe**⁺ are even much less specific than those with **Cr**⁺ which is in distinct contrast to the ethylene generation from **7-M**⁺ for which the opposite holds true⁹⁾. Similarly, the **Ni**⁺ complex of **7** is prone to undergo extensive rearrangements prior to propene loss and, as already described⁹⁾, also to ethylene elimination.

Although no quantitative analysis of the data given in Table 1 is yet possible, we note from the spectra of **7a, b, d, f** that **Fe**⁺ and **Ni**⁺ clearly favour path **a** over **b** which is in distinct contrast to **Cr**⁺.

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CAS Registry Numbers

Cr[⊕]: 14067-03-9 / **Fe**[⊕]: 14067-02-8 / **Ni**[⊕]: 14903-34-5 / 1,7-octadiene: 3710-30-3

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⁷⁾ The complexes **8** were generated by electron-impact ionization (100 eV) of a 10:1 mixture of **7** and a transition-metal-containing precursor suitable to generate **M**⁺ [e.g. **Fe**(CO)₅, **Ni**(acac)₂, or **Cr**(acac)₃, respectively] in the ion source of a modified ZAB mass spectrometer having *BEBE* configuration (*B* stands for magnetic and *E* for electrostatic sector). Complexes **8** were accelerated to 8 keV kinetic energy and mass-selected by *B*(1)*E*(1); unimolecular dissociations occurring in the field-free region between *E*(1) and *B*(2) were recorded by scanning *B*(2). All three metal ions **Fe**⁺, **Ni**⁺, and **Cr**⁺ give rise to abundant signals due to the loss of **C**₃**H**₆, which presumably corresponds to propene, from **8**: 50% total fragment ions for **7-Fe**⁺, 69% for **7-Ni**⁺, and 15% for **7-Cr**⁺.

⁸⁾ **Fe**⁺-mediated ring opening of cyclooctene → 1,7-octadiene was suggested (but not unambiguously proven) by: D. A. Peake, M. L. Gross, *Organometallics* **5** (1986) 1236.

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