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Homologation of Olefins with Methane on Transition Metals

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Abstract: Alkylation of olefins using methane has been realized on transition metal catalysts. The main problem is to get methane dissociatively adsorbed together with an olefin. This is due to the difficult activation of the strong tetrahedral C–H bonds of methane. To react methane with an olefin, a reaction sequence is used consisting of three steps. First methane is dissociatively adsorbed between 600 and 800 K on a reduced transition metal catalyst. After cooling, an olefin is coadsorbed on a reduced transition metal catalyst. Dissociative methane adsorption

Introduction

Methane homologation is of interest because of the many reactions that proceed via CH activation or carbon–carbon bond formation. Selective methane activation is difficult owing to the strong tetrahedral C–H bonds that lack polarity, and the ease of consecutive reactions of the resulting CH4 groups. Many different approaches have been developed in the activation of C–H bonds in alkanes, using organo-metal systems,1−4 heterogeneous catalysts,5−9 gas-phase metal ions,10 homogeneous catalysis,10,11 or biochemical systems.12 On transition metals the mechanism of dissociative alkane adsorption has been extensively studied on single crystals.13−18 The activity for metal films to activate methane at temperatures starting at 400 K was demonstrated by Bond19 and Frennet20 from the methane–deuterium exchange reaction. Dissociative methane adsorption on transition metal catalysts has a relative low activation energy (25−60 kJ/mol).20,21,22,26 However, to realize reasonable sticking coefficients for chemisorption, methane has to be activated.23−25 Dissociative methane adsorption at high temperature results mainly in unreactive coke formation.26,27 At mild conditions alkanes can be activated selectively with organo-metal complexes.1−3,28 In such a reaction the metal center (M) of the complex is able to interact with an alkane (R−H) and can finally insert into the C–H bond according to R−H + M → R−H−M → R−M−H.

Recently it has been found that hydrocarbons can be formed when methane is activated on a Ni single crystal,20 or on supported metal catalysts.21,22 We have shown previously24,25 that when methane is activated thermally under mild conditions, a surface C2 intermediate can be generated that is able to produce C2+ hydrocarbons upon hydrogenation. This occurs according to a Fischer–Tropsch synthesis type mechanism for carbon–carbon bond formation.25 O’Donohoe showed that the direct homologation of alkanes to a higher homologue is possible on tungsten catalysts.26,27 Also oxidative methylation of propane to butene has been reported28,29 on rare earth oxides. Alkylation of olefins with methane to an alkane with one extra carbon atom is thermodynamically possible below 500 K in one step.30 This reaction has been found to occur using superacids as catalysts.31 Syskin and Mayer32 converted methane–ethene

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(10) Ohl, Ch. A. Top. Curr. Chem. 1979, 80, 17.
mixtures to propane with a selectivity of 40-60%, using TaF$_5$-HF at 40 °C and 1 MPa. Olah used superacids immobilized on alumina. At 70 °C he reached a conversion of 38% with respect to ethene with a feed of CH$_4$/C$_2$H$_4$ of 9:1 mol/mol. Olah et al. showed in a reaction with 13C$_2$H$_4$ that under mild conditions, that 13C$_2$H$_4$ was formed selectively, when the methane/ethene ratio is above 100. Scurrell’s indicated that these systems may not be truly catalytic, and some fluorine loss from the catalyst may occur during the reaction. Although the solid superacids are used are much more environmentally friendly than homogeneous acids, the use of HF to activate these systems remains a drawback.

On heterogeneous metal catalysts, the direct conversion of methane with ethene has not yet been realized. Indirect conversion routes have been proposed on nickel catalysts. Löffler et al. performed a reaction with methane and cyclopentene to benzene and toluene at 310 °C. They repeated the reaction with 13CH$_4$ and were not able to detect incorporation of 13C into the reaction products. However, when the nickel oxide catalyst was reduced at a higher temperature with 13CH$_4$ before the reaction, 13C incorporation in benzene and toluene could be demonstrated to a modest extent. Ovales et al. reported the conversion of methane with propane to isobutane at 350 °C on a silica-supported nickel catalyst. They reduced the nickel oxide catalyst with methane at 600 °C for 8 h before the reaction. When the methane was substituted by nitrogen, the butane yield decreased, a process that is reversible. However, at 350 °C the thermodynamics are not favorable for the reaction of methane and propane to butane.

Previously the incorporation of CH$_2$ species from other molecules into ethene have been demonstrated using organo-metal complexes. Also from alkene addition experiments in the Fischer–Tropsch reaction, it is known that adsorbed olefins can undergo chain growth, resulting in longer hydrocarbons. A similar principle is applied here to incorporate surface carbon from methane into co-adsorbed olefins.

One of the main problems in the conversion of methane together with olefins on transition metals is the low sticking coefficient for dissociative methane adsorption compared to that of alkene adsorption. This prevents the simultaneous adsorption of methane and an olefin. To realize their co-adsorption, methane should not be adsorbed together with other reactants, but should be activated in a separate step. To achieve this, we developed a catalytic cycle in which the reactants are adsorbed separately at different temperatures (see Figure 1).

In the first step methane is thermally activated by dissociative adsorption on a reduced transition metal catalyst at a temperature between 200 and 550 °C. In the second step an olefin is co-adsorbed on the reduced ruthenium catalyst at a temperature between 20 and 100 °C. The ruthenium catalysts were dried at 110 °C and reduced in helium as quickly as possible to avoid “ageing” of the surface carbon. In the third step both hydrocarbon fragments are hydrogenated, forming a higher homologue.

This reaction sequence provides an overall reaction path for alklylation reactions using methane. Here we discuss the results for the reaction of methane with ethene, acetylene, and propene to form propane and butane, respectively. To prove that methane is actually incorporated into the reaction products, the reactions were repeated with 13C-labeled methane.

**Experimental Section**

**Catalysts.** A 5 wt % ruthenium catalyst and a 10 wt % cobalt catalyst were prepared by incipient wetness impregnation of Grace 332 type silica (300 m$^2$/g, pore volume = 1.65 mL/g, mesh size 75-125) with an aqueous solution of RuCl$_3$ (Drijfhout, Amsterdam) and Co(NO$_3$)$_2$·6H$_2$O (Merck), respectively. The catalysts were dried at 110 °C and reduced before each experiment in situ between 400 and 550 °C. The ruthenium catalyst was treated in a synthesis gas flow (H$_2$/CO = 2:1 at 100 kPa) for 30 min at 250 °C to increase its CO chemisorption capacity. The metal particle size as determined with transmission electron microscopy was 5.5 nm for the ruthenium and 8.5 nm for the cobalt catalyst. The active metal surface areas as derived from CO chemisorption (CO/Ru = 30% and CO/Co = 2.2%) indicate incomplete reduction of the cobalt catalyst.

**Experimental Conditions.** For each experiment 300 mg of the catalyst was placed in the reactor which consisted of a quartz tube (i.e. 10 mm). Methane adsorption was performed at 450 °C from a methane pulse to 90 s of 0.5% CH$_4$ in helium in a flow of 22.4 mL/min. After methane adsorption the catalyst was cooled to a temperature between 25 and 150 °C in helium as quickly as possible to avoid “ageing” of the surface carbon: typically the temperature was lowered within 100 s to 150 °C. Ethene, acetylene, or propene was adsorbed from pulses of 1.4 μmol between 25 and 150 °C. Subsequently, the adsorbed carbene...
surface species were hydrogenated in a flow of 22.4 mL/min of hydrogen at ambient pressure at the same temperature as the olefin adsorption. After this hydrogenation the temperature was raised at a rate of 20 °C/min to 550 °C in the same hydrogen flow, to remove carbonaceous residues. After cooling to 450 °C the cycle was repeated.

Analysis. During the first 2 min of hydrogenation, 15 × 0.2 mL of the reaction gases were stored in a 16 loop multiposition valve (Chrompack type ST34). The stored reaction gases were injected in a GC (CP 9000, Chrompack) and the reaction products were separated on a widebore plot Q column (25 m × 0.53 mm i.d.).

For the experiments with labeled methane (99% 13CH4 from Cambridge Isotope Laboratories), the stored reaction gases were separated on the same column, which was connected (splitless) with a coupling unit (Graphpack-3D-Saulenverbinder from Gerstel) to a fused silica capillary of 2 m (i.d. 100 μm). This capillary was directly introduced in the ion chamber of a high resolution mass spectrometer. During the analyses the masses between 10 and 60 Da were scanned every 1.5 s. For each component about 10–20 mass spectra were taken to calculate the average peak ratios. From these peak ratios the fraction of each labeled product was calculated (see Appendix). From the mass spectra the position of the 13C atom incorporated could be deduced.

Results

During the methane pulse at 450 °C all the methane is adsorbed on the ruthenium catalyst, resulting in a carbon surface coverage of about 20%. On the cobalt catalyst 60% of the methane is adsorbed. During the adsorption of ethene, acetylene, and propane between 25 and 150 °C, not all the reactants are adsorbed. A part of the olefin was autohydrogenated to the paraffin, while no olefin desorbed from the catalyst when adsorbed in small amounts. Especially when no methane was preadsorbed, olefine desorption was detected. Figure 2 compares the fractions of carbon adsorbed from a pulse of 1.4 pmol of ethene on a reduced ruthenium catalyst, with a pulse after pre-adsorption of 6.6 pmol of methane at 450 °C.

The fraction of adsorbed ethene is increased when surface carbon from methane is present on the catalyst surface. On the ruthenium catalyst more methane formation is observed during ethene adsorption than on cobalt. Above 100 °C methane is the only product desorbing from the ruthenium catalyst, while mainly ethene desors from the cobalt catalyst.

After the adsorption steps on the ruthenium catalyst 6.6 pmol of carbon from methane and 2.8 pmol of carbon atoms from ethene (1 pulse) are present on the catalyst surface. For the cobalt catalyst these figures are 4.0 and 1.7 pmol, respectively, due to the incomplete adsorption from the pulses. The amount of adsorbed carbonaceous surface species, which can be hydrogenated at a particular hydrogenation temperature, is shown in Figure 3 for the cobalt catalyst.

At a hydrogenation temperature above 100 °C most of the desorbing hydrocarbons originate from methane. Upon hydrogenation around 50 °C the hydrocarbons are formed from about the same amounts of adsorbed ethene and methane.

Figure 4 depicts hydrocarbon formation from surface carbon as a function of the exposure time to hydrogen at 40 °C, during the first 2 min. By integrating these curves, the selectivity can be calculated. This is shown in Figure 5 and is expressed on the basis of carbon efficiency. For butane and pentane the iso and normal products are taken together. Mainly linear hydrocarbons are formed.
Homologation of Olefins with Methane

Table I. Product Selectivity during Hydrogenation at 50 °C of Adsorbed Olefins with and without Preadsorbed Methane at 450 °C

<table>
<thead>
<tr>
<th>adsorbate methane ethane propane butane i/p C,</th>
<th>ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄ + C₂H₄</td>
<td>34</td>
</tr>
<tr>
<td>CH₄</td>
<td>20</td>
</tr>
<tr>
<td>CH₃C₂H₂</td>
<td>33</td>
</tr>
<tr>
<td>CH₄ + C₂H₆</td>
<td>8.3</td>
</tr>
<tr>
<td>CH₃ + C₂H₄</td>
<td>24</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>36</td>
</tr>
<tr>
<td>C₂H₄ + C₂H₆</td>
<td>1.9</td>
</tr>
</tbody>
</table>

*Sum of iso and n product.

On cobalt, at a low ethene adsorption and hydrogenation temperature, the selectivity to butane is remarkably high due to ethene dimethylation. When the hydrogenation temperature is raised, the methane selectivity increases owing to enhanced hydrogenolysis. The selectivity for the interesting reaction product propane is not a strong function of the temperature and has its maximum of 19% at 40 °C on the cobalt catalyst.

Figure 6 compares the amount of products formed during hydrogenation, after separate methane and ethene adsorption and their co-adsorption. As previously demonstrated,45,56 surface carbon from methane alone can be hydrogenation to C₂H₄ hydrocarbons. However, most of the dissociatively adsorbed methane reacts back toward methane. When ethene is co-adsorbed, the amount of methane formed as reduced and propane formation becomes significant. This indicates a reaction between adsorbed C₂ species from methane and co-adsorbed ethene forming propane. The ability to form propane from adsorbed methane and ethene was tested to different metal catalysts. The order of the selectivity for propane formation is Co, Ru > Pt, Ni, Rh > Ir > Re, Fe. Here only the results of the cobalt and ruthenium catalyst will be discussed.

As indicated in Table I, propane formation is also possible from adsorbed ethene via hydrogenolysis and homologation, resulting in methane and propane. Such disproportionation reactions have been extensively studied by Baet and co-workers.55-60 To distinguish this reaction from methane incorporation into adsorbed ethene, experiments with ¹³C-labeled methane were performed. Therefore, 6.6 μmol of ¹³CH₄ was pulsed at 450 °C over the catalyst and 5.2 μmol of unlabeled ethene, acetylene, or propene was co-adsorbed at 50 °C. The product selectivities of the experiments performed under those conditions are shown in Table I.

The reactions were repeated using ¹³CH₄ and the products were analyzed for the presence of ¹³C atoms. Of interest is the fraction of ¹³C incorporated in the alkylated reaction products. This was measured for the different labeled isotopes and is shown in Table II.

The labeled ¹³C atom from methane is added to adsorbed acetylene, ethene, and propene resulting in a product with one ¹³C atom from methane and ¹³C atoms from the olefin. This is shown by the underlined figures in Table II. As deduced from the fragment mass spectra, the labeled ¹³C atom in the singly labeled products is the primary atom in propane and butane. The reaction products propane and butane are also formed exclusively from ¹³C atoms from the adsorbed olefin due to auto-homologation. Apparently, ¹³C surface species from methane compete with ¹³CH₄ species generated by olefin hydrogenolysis for carbon incorporation.

Figure 7 shows the fraction of products containing one ¹³C atom, as a function of the hydrogenation time. The fraction of ¹³C in propane is a slight function of the hydrogenation time. The fraction of ¹³C in the product reaction increases a little as a function of time in nearly all the experiments with labeled methane.

Discussion

Ad sorption. Dissociative methane adsorption can result in three types of surface carbonaceous species. They differ in their hydrogenation temperature61,62 and have been identified as carbidic (C₃), amorphous (Cₓ), and graphitic (C₄) with AES63,64 and NMR.65 Under the particular methane adsorption conditions used here, about 60% of the surface carbon species from methane on Ru and 40% on Co consist of reactive carbidic Cₓ that is able to react below 100 °C with hydrogen to hydrocarbons. The less reactive C₃ and reactive Cₓ species can be removed during temperature-programmed hydrogenation. Up to a hydrogenation temperature of about 240 °C some Cₓ hydrocarbon formation is observed, while at higher temperatures only methane is formed.

The differences in adsorption probability of olefins, with and without the pre-adsorption of methane (Figure 2), might suggest a direct interaction between adsorbed surface carbon and the co-adsorbed olefin. However, concerning the ethene adsorption mechanism, this appears not to be the case. The mechanism of adsorption of ethene on reduced transition metals has been studied on single crystals.66-68 Chemisorbed ethene loses one or more

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The formation of Cg.56

The results are weighted averages of the analyses of 6 to 13 loops. For calculations, see Appendix.

hydrogen atoms at temperatures above room temperature and is adsorbed like an ethyldiene (C2H2), vinylidine (C2H=), or acetylide (C=C) surface species.9-11 Because of the low temperature, the resulting surface hydrogen does not desorb but is used to hydrogenate other ethene molecules to ethane in an auto-hydrogenation reaction. The desorbing products consist of only methane and ethene; no trace of ethene was detected at the low ethene surface concentrations applied. When surface carbon from methane is present, the free forming hydrogen atoms from ethene are used to form CH3 surface species, instead of forming ethene from ethene. This decreases the formation of ethene and enhances the fraction of ethene that remains adsorbed.

**Hydrogenation.** The optimum temperature for hydrogenation of surface carbon depends on the amount of surface species that can be hydrogenated and on the product selectivity (Figures 3, 4, and 5). In general, the selectivity to propane and butane is high at low hydrogenation temperature, while at a hydrogenation temperature about 80 °C, more surface carbon can be hydrogenated. The optimum hydrogenation temperature is about 50 °C. This is the temperature at which the experiments with labeled methane were done. At this temperature about equimolar amounts of adsorbed methane and olefins are hydrogenated on both catalyst systems. These amounts correspond to a carbon surface coverage of about 11% for both methane and alkene (normalized on the CO chemisorption capacity). At higher surface coverages, surface carbon becomes less reactive because of the enhanced formation of C8p.

Table I shows that, upon hydrogenation of adsorbed olefins, the selectivity for methane formation is higher on cobalt than on ruthenium. This result is in agreement with earlier observations,23,24 where it has been shown that ruthenium is the most active metal for hydrogenolysis. At 50 °C the clean surface of the well-reduced ruthenium catalyst has a remarkably high activity for hydrogenation. However, 30-50% of the homologated olefins contain only 1C, and thus originate entirely from the initial olefins. This means that C-C bond formation from C8 intermediates, generated from methane deposition or from alkene hydrogenolysis, occurs with about the same probability. Because the surface concentrations of the reacting methane and olefin fragments are the same, this indicates that the C8 intermediates involved are very similar. They probably both form carbon–carbon bonds according to a Fischer–Tropsch-like reaction mechanism.

Some additional experiments were done to study the influence of the olefin hydrogenation temperature and the ratio of adsorbed methane/olefin. When less ethene was pulsed and the ethene adsorption and hydrogenation temperature were decreased to 25 °C, the fraction of singly labeled 13C propane increased to 76% on the ruthenium catalyst. Because of the lower temperature, the rate of hydrogenolysis decreases. This reduces the amount of 13C surface fragments, resulting in an enhanced fraction of propane from [13C]methane and [13C2]ethene. The rate of hydrogenolysis is much lower on the cobalt catalyst. At 25 °C no methane formation is observed when adsorbed ethene is hydrogenolysed. However, in the reaction of 13CH4 with ethene, only 66% of the propane formed is singly labeled, while still 30% consists of only 13C from ethene. This suggests that either ethene reacts toward propane and methane, or that singly labeled propane can exchange its 13C carbon atom with a 12C from ethene, resulting in [13C–12C2] ethene. The latter compound does not appear in the gas phase, but can be dimerized to singly or doubly labeled butane, which butanes are formed in low fractions.

In Figure 2, however, 30-50% of the homologated olefins contain only 1C, and thus originate entirely from the initial olefins. This means that C-C bond formation from C8 intermediates, generated from methane deposition or from alkene hydrogenolysis, occurs with about the same probability. Because the surface concentrations of the reacting methane and olefin fragments are the same, this indicates that the C8 intermediates involved are very similar. They probably both form carbon–carbon bonds according to a Fischer–Tropsch-like reaction mechanism.

**Experiments with Labeled Methane.** Table II shows that labeled methane can be incorporated into co-adsorbed olefins, resulting in the reaction products propane and butane. This demonstrates alklylation of olefins with methane according to the reaction cycle in Figure 8. Methation mechanism according to which [13C]propene may exchange a carbon atom with a 13C from methane. The hydrogen atoms are not drawn (M is an active center consisting of one or more metal atoms).

<table>
<thead>
<tr>
<th>precursor</th>
<th>methane</th>
<th>ethane</th>
<th>propane</th>
<th>n-butane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetylene</td>
<td>95</td>
<td>83</td>
<td>2</td>
<td>12</td>
</tr>
<tr>
<td>Ethene</td>
<td>99</td>
<td>89</td>
<td>0</td>
<td>12</td>
</tr>
<tr>
<td>Propene</td>
<td>98</td>
<td>61</td>
<td>9</td>
<td>30</td>
</tr>
</tbody>
</table>

Table II. Relative Frequency of Different 13C Isotopically Labeled Reaction Products

The results are weighted averages of the analyses of 6 to 13 loops. For calculations, see Appendix.

**Figure 8.** Methation mechanism according to which [13C]propene may exchange a carbon atom with a 13C from methane. The hydrogen atoms are not drawn (M is an active center consisting of one or more metal atoms).

on MoO₃ catalyst. They demonstrated that surface carbon species involved in metathesis are different from the intermediates active in the Fischer–Tropsch reaction. The hydrocarbon isomerization reactions as reported on platinum⁷⁷–⁷⁹ are relatively slow on these catalysts.

It is possible to calculate the selectivity for hydrogenolysis and homologation of the adsorbed olefins in the presence of ¹³C from methane from Tables I and II, by not taking into account the molecules containing ¹³C atoms. The selectivity pattern appeared to be about the same as that of the solely adsorbed olefins. This indicates that the selectivities for hydrogenolysis, homologation, and dimerization are not influenced by surface carbon species from methane. In particular, for hydrogenolysis this was unexpected, because surface carbon should decrease the amount of free metal ensembles necessary for hydrogenolysis. Apparently the carbon surface coverages applied (~20%) are too low to change the mentioned rates significantly.

**Isobutane/n-Butane Ratio.** During the hydrogenation of carbonaceous intermediates from methane and olefins at 50 °C, the selectivity for butane formation varies from 5 to 60%. Most of the butane is n-butane but some isobutane is formed. In relation to isobutane formation, differences in the mechanistic routes of formation are of interest. A comparison of the fraction of ¹³C in n-butane and isobutane in the hydrogenation reaction of adsorbed ¹³C with ethene or propene is given in Table III.

Owing to the low selectivity, the fraction of ¹³C in isobutane could not be determined with great accuracy. The incorporation of ¹³C in isobutane formed from ethene is more dominant than in n-butane, because the latter is mainly formed by dimerization of ethene. ISO- and n-butane are not in a dynamic equilibrium, and their routes of formation are probably different. For the incorporation of ¹³C in propene to form iso- and n-butane, no significant differences were found. This indicates that surface carbon generated from propene dissociation reacts similarly as surface carbon from methane.

When the carbon surface coverage is higher, adsorbed propene species react to a larger extent to isobutane: the ratio of iso- /n-butane increases from 0.08 to 0.16 on cobalt (see Table I). This indicates that in the formation of isobutane a surface carbon atom is involved. The ratio of iso- /n-butane from only surface carbon from methane is higher (0.30) than that with adsorbed propene. Adsorbed propene reacts mainly toward n-butane.

### Table III. Percentage of Singly ¹³C-Labeled Iso and n-Butane

<table>
<thead>
<tr>
<th>precursors</th>
<th>iso-C₄</th>
<th>n-C₄</th>
<th>iso-C₄</th>
<th>n-C₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>¹³CH₄ + C₂H₄</td>
<td>50-70</td>
<td>14</td>
<td>60-80</td>
<td>15</td>
</tr>
<tr>
<td>C₂H₄ + C₂H₆</td>
<td>40-80</td>
<td>73</td>
<td>30-50</td>
<td>45</td>
</tr>
</tbody>
</table>

The exchange of carbon atoms according to a metathesis reaction cycle in which methane is separately adsorbed. In this way methane can be used as an alkylating agent. This is demonstrated for the incorporation of methane into ethene, acetylene, and propene. The reaction products propane and butane can be formed also via auto-homologation. The comparable reaction rates of self-homologation and methane incorporation indicate that the C₂ intermediates involved are similar; they are both related to the CH₃ fragments active in the Fischer–Tropsch reaction.

The exchange of carbon atoms according to a metathesis reaction does not occur on the ruthenium catalyst, while it cannot be excluded on cobalt. The cobalt catalyst has a remarkably high selectivity for dimerization of adsorbed ethene.

### Appendix

#### Calculation of Isotopic Distributions from Mass Spectra.

An alkane with n carbon atoms either ¹²C or labeled ¹³C, can have n + 1 differently labeled isotopes: unlabeled, singly ¹³C labeled, up to n times labeled alkane (not taking into account the different positions of the ¹³C atom). It is possible to calculate the fraction of each differently labeled isotope from a mass spectrum. This is not trivial because the mass spectrum of the unlabeled alkane disturbs an easy calculation.⁸⁸ Here we present an algorithm to deduce these fractions from the mass spectrum. Propane is taken as an example, while problems are identical for C₄ with n > 3. Propane can have four types of different labeled isotopes: ¹²C₃, ¹²C₂¹³C, ¹²C–¹³C–¹³C, and ¹³C₃. Their relative frequency are indicated with f₁ to f₄. To calculate f₁ to f₄ one has to know the

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Aerobic Oxidative Dehydrogenations Catalyzed by the Mixed-Addenda Heteropolyanion PV₂Mo₁₀O₄₀⁵⁻: A Kinetic and Mechanistic Study

Ronny Neumann* and Michal Levin

Contribution from the Casali Institute of Applied Chemistry, Graduate School of Applied Science and Technology, The Hebrew University of Jerusalem, Jerusalem, Israel 91904. Received December 31, 1991

Abstract: The aerobic oxidative dehydrogenation of α-terpinene to p-cymene catalyzed by the mixed-addenda heteropolyanion PV₂Mo₁₀O₄₀⁵⁻ has been used to investigate the oxidation mechanism catalyzed by this class of compounds. The kinetics of the reaction show it to be zero order in α-terpinene, first order in dioxygen, and second order in the heteropolyanion catalyst. Further catalytically important subclasses of the Keggin compounds are the mixed-addenda anions XM'₉M₁₂⁻O₆₀₅⁻ (2), where for example X = P, M' = V, and n = 1, 2, and the transition metal substituted Keggin compounds XM'(L)₁M₁₁O₃₉ (3), where M' is a transition metal such as Mn, Co, Cu, Ru, etc. and L is a ligand such as H₂O, OH, or pyridine, among others.

Introduction

Since the discovery in 1826 by Berzelius of the first heteropoly compound,¹ the vast field of heteropolyanion chemistry has been centered mostly around the preparation, structure, properties, and analytical chemistry applications of these compounds.² Heteropoly compounds are soluble polyoxometalates of anions having the general formula [XₙMₘOₜ]ᵢ⁻ (x ≤ m), where X is a heteroatom and M is an addenda atom. A common and important class of these salts and those used in the majority of catalytic applications is the Keggin compounds (Figure 1), with the general formula XMₙOₜ₀⁺ (1) (X = P, Si, As, Ge, B, etc.; M = Mo, W).

Further catalytically important subclasses of the Keggin compounds are the mixed-addenda anions XM'₉M₁₂⁻O₆₀₅⁻ (2), where for example X = P, M' = V, and n = 1, 2, and the transition metal substituted Keggin compounds XM'(L)₁M₁₁O₃₉ (3), where M' is a transition metal such as Mn, Co, Cu, Ru, etc. and L is a ligand such as H₂O, OH, or pyridine, among others.

Interest in heteropoly compounds as homogeneous liquid-phase oxidation catalysts is only a recent development that has been fueled by the inherent stability of these compounds to strongly oxidizing conditions as opposed to other effective and widely studied catalysts such as metalloporphyrins,³ which always decompose in the presence of oxidants.⁴ Importantly, it has also

[^3]: Ortiz de Montellano, P. R. Cytochrome P-450; Plenum: New York, 1986.
[^4]: (4) Recently efforts have been made to increase the stability of porphyrins by halogenation of the porphyrin ring: (a) Traylor, T. G.; Tsaidimos, G. A. Top. Curr. Chem. 1987, 26, 1339. (b) Traylor, T. G.; Byun, Y. S.; Traylor, P. S.; Batisomin, P.; Mansuy, D. J. Am. Chem. Soc. 1991, 113, 7821.