

## Activation of C–C bonds in alkanes and cycloalkanes by Ziegler-type systems

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(Received February 20th, 1987; in revised form May 1st, 1987)

### Abstract

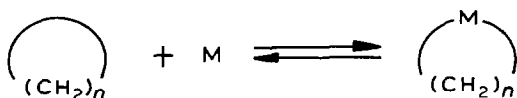
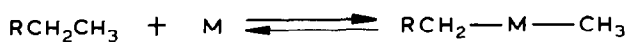
Interaction of rhenium carbonyl or carbonyl-hydride complexes ( $\text{Re}_2(\text{CO})_{10}$ ,  $\text{Re}_3\text{H}_3(\text{CO})_{12}$ ,  $\text{Re}_4\text{H}_4(\text{CO})_{12}$ ) with organoaluminium compounds ( $\text{Et}_3\text{Al}$ ,  $\text{Bu}^i_2\text{AlH}$ ) in a saturated hydrocarbon medium at 150–180 °C and an initial  $\text{H}_2$  pressure of 50 atm. leads to the formation of active catalysts for alkane and cycloalkane hydrogenolysis. At 180 °C the hydrocarbon conversions are close to 100% after several hours, with one mole of rhenium compound catalyzing the transformations of hundreds of moles of hydrocarbon. The activity of the catalytic system strongly depends on the ratio of its components. At the early stage, the cleavage of terminal  $\text{CH}_2\text{--CH}_3$  bonds of initial n-alkanes is the main direction of reaction, while cycloalkanes undergo, first, ring opening. The data obtained show that the catalysts found are organometallic hydride rhenium complexes rather than rhenium metal.

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### Introduction and an approach to the problem

The activation and cleavage of carbon–carbon bonds in saturated hydrocarbons is an important scientific and technological problem. However, the splitting of thermodynamically stable nonpolar  $\sigma$ -bonds in hydrocarbon molecules lacking both lone electron pairs and low unoccupied orbitals, demands drastic conditions and occurs usually at high temperatures [1,2].

In the last three decades a great success has been achieved in application of transition metal complexes for activation of inert covalent bonds, such as H–H [3,4], Si–H [5–7], Si–C [8,9], C–H (including C–H bonds in paraffins) [10–13] etc. However, all known catalytic transformations of alkanes and cycloalkanes under the action of transition metal complexes in the liquid phase proceed with participation of only C–H bonds. Catalytic cleavage of saturated hydrocarbon C–C bonds under the action of transition metal complexes is known only for strained cycloalkanes and polyhedral alkanes [12].



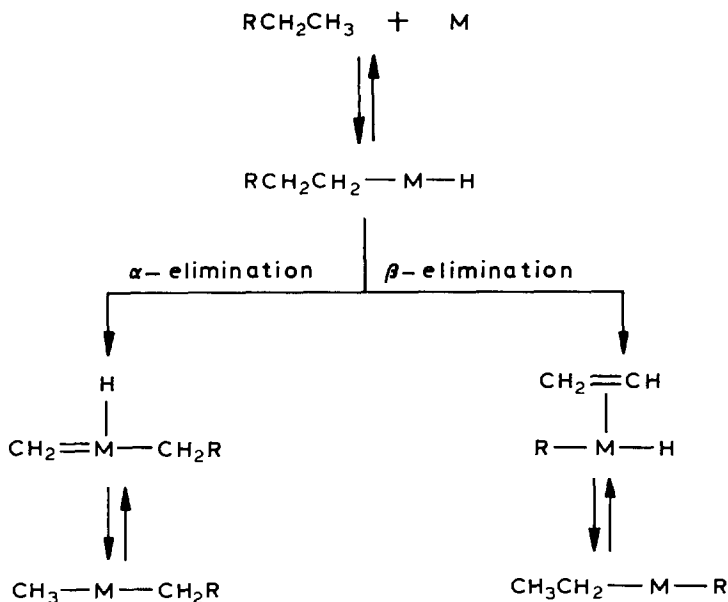
Scheme 1

Some general considerations lead us to propose two pathways for C–C bond activation in saturated hydrocarbons by coordinatively unsaturated transition metal complexes. The first pathway involves direct insertion of a metal complex into the C–C bond (Scheme 1). The second possibility involves oxidative addition of the C–H bond to the metal centre of the complex followed by intramolecular cleavage of a C–C bond in this complex [14]. Several modes of intramolecular C–C bond cleavage in  $\sigma$ -alkyl hydride complexes can be proposed (Scheme 2).

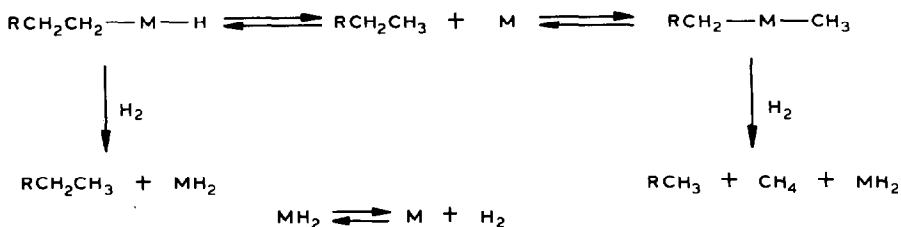
The assumptions that  $\alpha$ - and  $\beta$ -C–C bonds fragment are based on some gas phase reaction data [15], on known liquid phase cleavages in metallacycloalkanes [16] and on  $\beta$ -methyl transfer in an alkylanthanide complex [17].

Taking into account the large steric screening of C–C bond atoms in paraffins we can formulate the following requirements for activation and cleavage of such bonds by transition metal complexes:

- (1) rather high dissociation energy of the M–C bond;
- (2) low oxidation state of the metal, i.e. its facile oxidative addition;
- (3) low coordination number of the metal, which minimizes steric hindrance to attack on the C–C bond;



Scheme 2



Scheme 3

(4) only small ligands, which provide the least steric screening of the metal atom. Typical examples are H and CO.

Fulfillment of these requirements would facilitate both C-H and C-C bond activation. The C-C bond cleavage is further favoured by removing the intermediate product  $\text{RCH}_2-\text{M}-\text{CH}_3$  (Scheme 3). Hydrogenation of  $\text{RCH}_2-\text{M}-\text{CH}_3$  accomplishes this.

### Results and discussion

In the search for catalytic systems satisfying the above requirements we examined a range of various Group VI-VIII transition metal derivatives, such as carbonyls, carbonyl hydrides, halides, oxides and Ziegler-type systems with saturated hydrocarbons under hydrogen.

We have found [18] that solubilized rhenium carbonyl and carbonyl hydride complexes, such as  $\text{Re}_2(\text{CO})_{10}$ ,  $\text{Re}_3\text{H}_3(\text{CO})_{12}$ , and  $\text{Re}_4\text{H}_4(\text{CO})_{12}$  in combination with organoaluminium compounds ( $\text{Et}_3\text{Al}$ ,  $\text{Bu}_2^i\text{AlH}$ , etc.), in fact, can activate C-C bonds and catalyze hydrocracking of alkanes and cycloalkanes, such as hexane, octane, cyclopentane, methylcyclopentane, cyclohexane and cyclodecane. The reactions proceed in the hydrocarbon at 150-180°C at an initial  $\text{H}_2$  pressure of 50 atm. At 180°C the hydrocarbon conversions are close to 100% after several hours, with one mole of the rhenium compound catalyzing the transformation of hundreds of moles of hydrocarbon (examples are shown in Table 1).

The activity of the catalytic system strongly depends on the ratio of its components. Thus, the activity of the catalyst formed by interaction of  $\text{Re}_2(\text{CO})_{10}$  with  $\text{Bu}_2^i\text{AlH}$  attains a maximum at an atomic Al/Re ratio equal to 3. However, when the ratio is increased to 5.5 or decreased to 1.5, the active catalyst is not formed at all (see Fig. 1). It should be noted that neither organoaluminium compounds alone nor various rhenium complexes (such as  $\text{Re}_2(\text{CO})_{10}$ ,  $\text{Re}_3\text{H}_3(\text{CO})_{12}$ ,  $\text{Re}_4\text{H}_4(\text{CO})_{12}$ ,  $\text{CpRe}(\text{CO})_3$ , and  $\text{Na}_2\text{ReH}_9$  in the absence of organoaluminium compounds) show any activity in alkane cleavage at 180°C over 40 hours, but that a homogeneous catalytic system based on  $\text{ReH}_7(\text{PR}_3)_2$  was successfully employed for paraffin C-H bond activation [19].

It is known that rhenium metal, in contrast to platinum metals, does not catalyze the hydrogenolysis of C-C bonds in saturated hydrocarbons up to 300°C [20]. In agreement with these data our special experiments demonstrated rhenium black [21] to exert no activity in these reaction up to 300°C.

The main products of the early stage conversions of n-alkanes, catalyzed by the systems, found are methane and linear alkanes with one carbon atom less than the

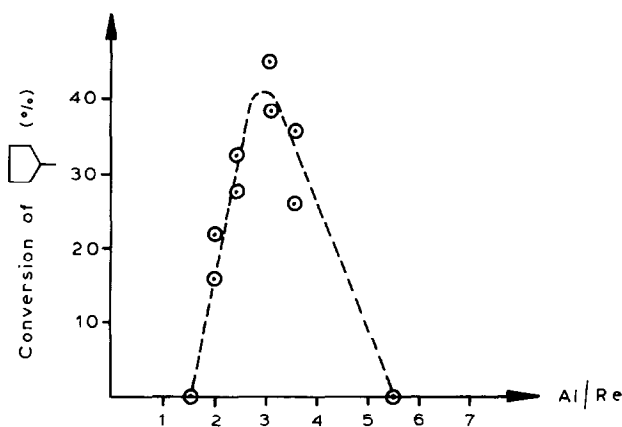
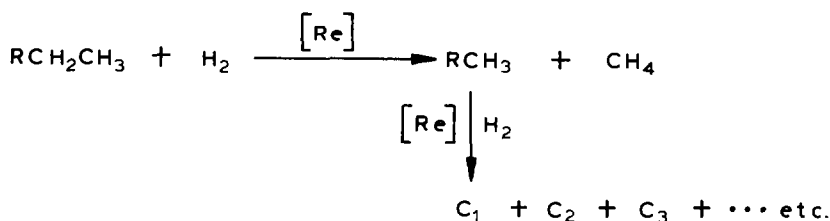


Fig. 1. Dependence of the catalytic activity of  $\text{Re}_2(\text{CO})_{10} + \text{Bu}_2\text{AlH}$  systems on the Al/Re atomic ratio.

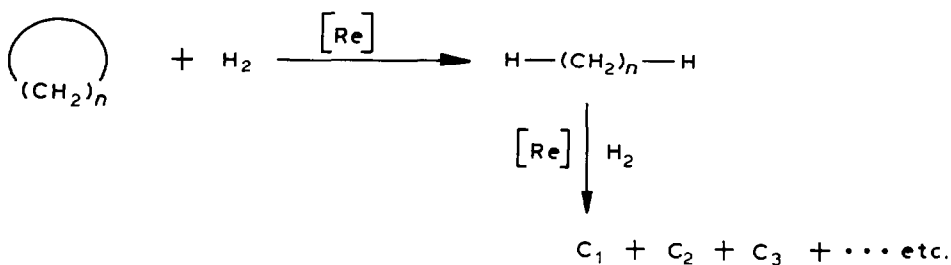


Scheme 4

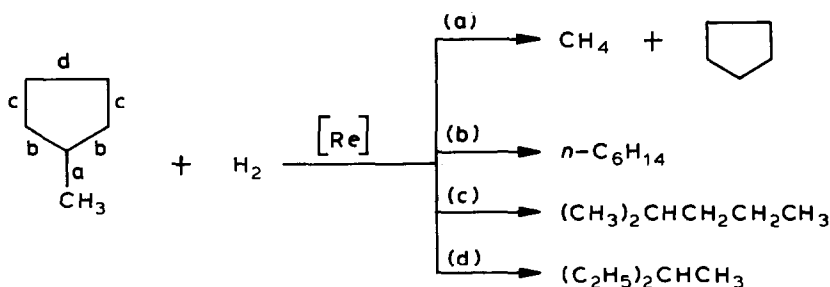
starting paraffin. Further the products of subsequent hydrogenolyses are formed (Scheme 4). Thus at the early stage of reaction, cleavage of terminal  $\text{CH}_2\text{-CH}_3$  bonds is the main step of reaction.

Cycloalkanes undergo, first, ring opening to linear alkanes with the same number of carbon atoms, then, products of their further stepwise hydrogenolysis are formed (Scheme 5).

Under these conditions the hydrogenolysis of methylcyclopentane yields three isomeric hexanes, viz. 2-methylpentane, 3-methylpentane and n-hexane in a ratio of 2/1/0.04. Hence in methylcyclopentane the least screened C-C bonds are preferentially cleaved (Scheme 6).



Scheme 5



Scheme 6

The above hydrogenolysis catalysts are X-ray amorphous pyrophoric black powders that are insoluble in conventional organic solvents, such as hydrocarbons, ether, MeCN, THF. Therefore the catalytic process observed is heterogeneous. The catalysts contain a remarkably large amount of organic material. Elemental analyses show that the catalysts consist of Re (~ 70%), Al (~ 16%), C (4–9%) and H (1–2%), depending on preparative details. Hydrogenation of the catalyst in a hydrogen stream at 100–200°C produces C<sub>1</sub>–C<sub>5</sub> alkanes (mainly C<sub>4</sub>–C<sub>5</sub>). Aqueous acids, such as H<sub>2</sub>SO<sub>4</sub> and CH<sub>3</sub>COOH, decompose the catalyst with evolution of hydrogen and formation of the same C<sub>1</sub>–C<sub>5</sub> alkanes along with a small amount of X-ray amorphous rhenium metal, as indicated by elemental analysis and ESCA\*. A clear, dark brown aqueous solution (obtained after catalyst acidification) does not separate after centrifugation at 360 g for one hour. Action of KOH on this solution in air leads to precipitation of KReO<sub>4</sub>.

The IR spectra of the catalysts have two weak bands at 1900 and 2025 cm<sup>-1</sup> which may be attributed to Re–H rather than Re–CO bond vibrations as, according to the EXAFS-spectroscopy\*, Re atoms in the catalysts bear no CO ligands.

The EXAFS Re–L<sub>III</sub>-edge spectra of the catalysts show that each rhenium atom is bonded to 2–3 carbon atoms at Re–C distance of 2.18 Å and to one or two metal atoms at Re–M (M = Re or Al) distance of 2.6–2.7 Å.

Thus, all data show that the paraffin hydrogenolysis catalysts found are organometallic hydride rhenium complexes rather than rhenium metal. Further investigations are necessary in order to elucidate the catalytic structure, the nature of the catalytic centre and the reaction mechanisms.

## Conclusion

Examples of catalytic cleavage of C–C bonds in ordinary alkanes and cycloalkanes under the action of the heterogeneous catalysts based on Ziegler-type systems have been found. The preliminary data show that these heterogeneous catalysts are organometallic hydride rhenium complexes rather than rhenium metal. These results

\* ESCA = electron spectroscopy for chemical analysis.

\*\* EXAFS = extended X-ray absorption fine structure.

Table 1  
Catalytic hydrocracking of alkanes and cycloalkanes by systems based on rhenium carbonyls and organoaluminum compounds (50 atm H<sub>2</sub>)

Run	RH	Catalyst <sup>a</sup>	RH/AIR <sub>3</sub> / R <sub>6</sub> L <sub>m</sub> (molar ratio)	Tem- pera- ture (°C)	Reac- tion time (h)	Conver- sion of RH (%)	Products, moles per mole of reacted RH <sup>b</sup>									
							C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	C <sub>5</sub>	C <sub>6</sub>	C <sub>7</sub>			
1	C <sub>6</sub> H <sub>14</sub>	Re <sub>2</sub> (CO) <sub>10</sub> + A	100/6/1	180	3	77	2.81	0.53	0.28	0.17	0.16					
2	C <sub>6</sub> H <sub>14</sub>	Re <sub>2</sub> (CO) <sub>10</sub> + A	100/6/1	150	3	16	1.39	0.28	0.15	0.21	0.57					
3	C <sub>8</sub> H <sub>18</sub>	Re <sub>2</sub> (CO) <sub>10</sub> + A	100/6/1	180	3	46	1.33	0.23	0.09	0.09	0.13	0.17			0.27	
4	C <sub>8</sub> H <sub>18</sub>	Re <sub>2</sub> (CO) <sub>10</sub> + A	100/6/1	180	5	65	1.56	0.30	0.16	0.16	0.18	0.18			0.22	
5	C <sub>8</sub> H <sub>18</sub>	Re <sub>2</sub> (CO) <sub>10</sub> + A	100/10/1	180	15	54	1.80	0.20	0.07	0.06	0.07	0.10			0.19	
6	C <sub>8</sub> H <sub>18</sub>	Re <sub>2</sub> (CO) <sub>10</sub> + B	190/10/1	180	15	48	2.00	0.46 <sup>c</sup>	0.11	0.15	0.16	0.18			0.27	
7	cyclo-C <sub>3</sub> H <sub>10</sub>	Re <sub>2</sub> (CO) <sub>10</sub> + A	100/6/1	180	3	93	0.89	0.17	0.11	0.16	0.43					
8	cyclo-C <sub>3</sub> H <sub>10</sub>	Re <sub>2</sub> (CO) <sub>10</sub> + A	100/6/1	150	3	16	0.08	0.02	0.01	0.09	0.93					
9	cyclo-C <sub>3</sub> H <sub>10</sub>	Re <sub>2</sub> (CO) <sub>10</sub> + A	100/6/1	150	5	27	0.11	0.02	0.02	0.08	0.83					
10	cyclo-C <sub>3</sub> H <sub>10</sub>	Re <sub>2</sub> (CO) <sub>10</sub> + A	100/9/1	180	15	94	0.61	0.12	0.08	0.14	0.46					
11	cyclo-C <sub>3</sub> H <sub>10</sub>	Re <sub>2</sub> (CO) <sub>10</sub> + A	200/9/1	180	7	56	0.39	0.06	0.04	0.05	0.64					
12	cyclo-C <sub>3</sub> H <sub>10</sub>	Re <sub>4</sub> H <sub>4</sub> (CO) <sub>12</sub> + A	200/12/1	180	15	84	0.98	0.16	0.13	0.07	0.58					
13	cyclo-C <sub>3</sub> H <sub>9</sub> CH <sub>3</sub>	Re <sub>2</sub> (CO) <sub>10</sub> + A	100/6/1	180	3	28	0.22	0.02	0.01	0.03	0.14	0.59				
14	cyclo-C <sub>3</sub> H <sub>9</sub> CH <sub>3</sub>	Re <sub>4</sub> H <sub>4</sub> (CO) <sub>12</sub> + A	200/12/1	180	15	82	0.94	0.10	0.04	0.07	0.19	0.50				
15	cyclo-C <sub>3</sub> H <sub>9</sub> CH <sub>3</sub>	Re <sub>3</sub> H <sub>3</sub> (CO) <sub>12</sub> + A	200/9/1	180	15	82	1.14	0.12	0.04	0.08	0.18	0.40				
16	cyclo-C <sub>8</sub> H <sub>12</sub>	Re <sub>2</sub> (CO) <sub>10</sub> + A	100/6/1	180	3	22	0.85	0.11	0.05	0.09	0.22	0.30				
17	cyclo-C <sub>10</sub> H <sub>20</sub>	Re <sub>2</sub> (CO) <sub>10</sub> + B	26/9/1	180	15	78	0.93	0.69 <sup>c</sup>	0.06	0.06	0.05	0.04	0.04			

<sup>a</sup> A = Bu<sub>2</sub>AlH, B = Et<sub>3</sub>Al; in the runs 1-4, 7-9, 13, 16 catalysts have been previously formed. <sup>b</sup> n-Alkanes, with the exception of runs 13-15. <sup>c</sup> Et<sub>3</sub>Al is also the source of ethane. <sup>d</sup> C<sub>8</sub>, 0.06; C<sub>9</sub>, 0.14; C<sub>10</sub>, 0.14.

draw us to believe in the possibility of creation of homogeneous catalytic systems based on coordinatively unsaturated transition metal complexes for activation of C–C bonds in alkanes and cycloalkanes.

## Experimental

All manipulations were conducted under argon using standard autoclave and Schlenk techniques. Gas liquid chromatography (GLC) analyses were performed in a Chrom-5 chromatograph using  $250 \times 0.3$  cm PAR-2 stainless steel column (temperature program 25–180 °C, 15 °C/min) for gaseous products and 1 m  $\times$  0.22 mm OV-101 glass open tubular column for liquid products. IR and EXAFS spectra of the catalysts suspensions in absolute Apiezon–Fett M were measured in air immediately after preparation of the samples.

Hydrocarbons were purified by a standard procedure and, dried, refluxed and distilled over  $\text{LiAlH}_4$  before using. Organoaluminium compounds were distilled in vacuo.

$\text{Re}_2(\text{CO})_{10}$  was purified by filtration of its pentane solution through an alumina layer followed by vacuum sublimation.  $\text{Re}_3\text{H}_3(\text{CO})_{12}$  was prepared by the direct hydrogenation of  $\text{Re}_2(\text{CO})_{10}$  in decalin [22] and purified by sublimation in vacuo and recrystallization from cyclohexane in an extractor.  $\text{Re}_4\text{H}_4(\text{CO})_{12}$  was prepared by hydrogenation of  $\text{Re}_2(\text{CO})_{10}$  in decalin [23] during 110 hours. All rhenium complexes were carefully dried in vacuo over  $\text{P}_2\text{O}_5$  prior to use.

*General procedure of paraffin hydrogenolysis.* To a mixture of  $\text{Re}_2(\text{CO})_{10}$  (0.5 mmol) and hydrocarbon (30 mmol) in a 50 ml stainless steel autoclave cooled with liquid nitrogen (avoiding condensation of argon) was quickly added a solution of  $\text{Bu}^i_2\text{AlH}$  (3 mmol) in the same hydrocarbon (20 mmol) and the pressure of  $\text{H}_2$  was brought up to 50 atm during 1–5 seconds. The mixture was warmed to room temperature with vigorous stirring (10 min). After keeping overnight, the mixture was heated at 180 °C over several hours (see Table 1). After cooling the gaseous products were distilled to a liquid nitrogen trap and analyzed by GLC. The liquid hydrocarbon products were distilled from the autoclave and analyzed by GLC using an internal standard. A new portion of hydrocarbon can be added to the remaining catalyst and the hydrocracking procedure can be repeated at 150–180 °C. No loss in the activity of the catalyst was observed during 100 hours.

## Acknowledgements

The authors are indebted to Drs. A.T. Shuvaev, B.Yu. Khel'mer, N.I. Puzynya and F.M. Ovsyannikov for the EXAFS investigations and helpful discussions.

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