

THE MICROWAVE PROMOTED CARBON CATALYZED PRODUCTION OF TERMINAL OLEFINS FROM LONG CHAIN ALKANES AND CARBON-CARBON CLEAVAGE REACTIONS OF ORGANIC MOLECULES

Dennis D. Tanner,¹ Qizhu Ding,¹ Pramod Kandanarachchi² and James A. Franz²

Contribution from the Department of Chemistry,
University of Alberta, Edmonton, Alberta, T6G 2G2, Canada
and
Pacific Northwest National Laboratory
Richland, WA 99352 USA

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ABSTRACT

The selective conversion of saturated linear hydrocarbons at ambient temperature to α -olefins and dihydrogen and other transformations of organic molecules involving the direct scission of carbon-carbon bonds are described. Activated wood charcoals containing trace metals were subjected to microwave radiation in the presence of liquid hydrocarbons at room temperature. Long-chain hydrocarbons were converted with high selectivity to a series of terminal olefins. For example, at less than 30% conversion, n-hexadecane yields n-C₃ to n-C₁₄ α -olefins and light gases, predominately ethylene, and dihydrogen. Extensive conversion of linear hydrocarbons leads to substantial yields of α -olefins, diterminal diolefins, and ethylene. Product distributions are consistent with a pathway for olefin formation from linear hydrocarbons at room temperature that does not involve free radical formation. The method is effective for carbon-carbon bond cleavage in and conversion of a wide array of linear and branched hydrocarbon feedstocks to hydrogen, ethylene, and olefins. Saturated organic hydrocarbons containing functional groups (-OH, -CN, -CO₂H, -CO₂CH₃) undergo carbon-carbon bond scission and olefin formation with substantially intact functional groups. Cyclic alkanes and terpenoid hydrocarbons under ring cleavage, contraction, and ring isomerization reactions. In the presence of small amounts of water, cycloalkanes are converted to cyclic alcohols and ketones. The method makes possible selective chemical transformations involving the direct cleavage of saturated carbon-carbon bonds at room temperature.

INTRODUCTION

The direct cleavage of strong carbon-carbon bonds to effect selective synthesis of lower molecular weight hydrocarbons is a primary goal of research in heterogeneous and homogeneous catalysis. Methods for the selective, direct cleavage of strong carbon-carbon bonds, particularly at ambient temperature and atmospheric pressure, are scarce. Most approaches involve some degree of thermal hydrocracking to effect strong bond scission and structural isomerization, or the involvement of transition metal catalysts capable of activation of a hydrocarbon via oxidative addition of a hydrocarbon C-H bond to a coordinatively unsaturated metal system. Previous work with microwave-activated catalysis has involved creation of high local temperature regimes leading to thermal cracking and reforming involving free radicals, ions, carbenes, atoms and other reactive intermediates. Solution phase microwave promoted chemical transformations have generally dealt with either dielectric heating of the substrate or catalyst,³ or with reactions carried out using a vapor phase plasma.⁴ These approaches using dielectric heating involve the creation of "hot spots" in the catalyst surface that promote chemical transformations through local high temperature regimes.⁵ Thus, thermolysis of methane over a glowing microwave catalyst produces ethylene, acetylene, propylene, hydrogen and soot reminiscent of simple thermal pyrolysis.^{3d} Under more controlled conditions of low power irradiation, ethylene and acetylene may be prepared from methane and hydrogen with significant selectivity.⁵ While previous studies have demonstrated that light organic gases can be converted under plasma initiation conditions, no previous work has explored the utility of microwave activated catalysis in bond-breaking transformations of large organic molecules and functionalized alkanes. Thus, in this work we present results of a study of low-power microwave irradiation of an activated carbon catalyst that leads to carbon-carbon bond cleavage and olefin formation from linear alkanes without formation of characteristic organic pyrolysis products. High yields of olefins and hydrogen result from a range of hydrocarbon precursors and functionalized hydrocarbons. Organic structures are demonstrated to exhibit significant chemical selectivity in carbon-carbon bond scission reactions, in part due to the ability of the liquid organic medium to rapidly quench high energy intermediates.

EXPERIMENTAL

Microwave Conversion of Hexadecane To Olefins. Hexadecane (2 g) was mixed with activated charcoal (0.5 g) in a reaction tube and subjected to microwave radiation (20 min) at 60% power

(ca. 30 watts) at 2540 MHz using the apparatus shown in Figure 2. The total volume of the gaseous products were measured by the gas burette, and both gaseous and liquid products were analyzed by GC, GC/IR and GC/MS. Products were identified by comparison of their GC retention times, GC/IR and GC/MS of authentic samples that were available. When the authentic samples were not available, products were identified by their GC/IR and GC/MS which showed similarities to those of authentic homologous compounds. Gaseous and liquid products are shown in Table 1.

Microwave Promoted Reaction of Polyethylene in the Presence of Wood Char. A sample of low density polyethylene (2 g) was heated to melt ($>130^{\circ}\text{C}$) and mixed with activated charcoal (0.5 g) and subjected to microwave radiation for 2 minutes. The products were identified by means of GC, GC/IR and GC/MS and comparison with authentic materials. With extended irradiation, the molten polymer could be completed converted to volatile products consisting primarily of ethylene, along with hydrogen, and minor yields of light olefins and hydrocarbons.

Microwave Promoted Conversion of Diacid Esters. Dimethyl-1,6-hexanedioic acid ester (Dimethyladipate). 0.1g of charcoal and 1 g of substrate were irradiated for 2 hours at 50W. The major products (30% conversion) were methyl acrylate, methyl butanoate, and methyl pentanoate, formed in the ratio 20:5:1. These products composed 85% of the product mixture. Minor products methyl propionate, methyl butanoate, and methyl pentanoate were formed as 15% of the reaction mixture. Hydrogen was not quantitated in the reaction. These results suggest that dimethyl adipate was cleaved to form methylacrylate with 65% selectivity. **Dimethylmalonate.** 0.15g wood char and 2.5 g substrate were irradiated for two hours. This resulted in less than 4% conversion to gaseous products and less than ca. 1% conversion to liquid products (methanol and methyl acetate). **Diethylsuccinate.** 0.15 g wood char and 2.5 g substrate were irradiated for two hours. About 10% conversion to gaseous products (CO_2 , CH_4 , C_2H_2 , C_2H_4) and 2% conversion to ethanol and ethylacrylate occurred.

Microwave Irradiation of Methyl Palmitate. Methyl Palmitate, 1 g and wood char, 0.1 g, were irradiated for 1 hour. Products included gases (C_2H_4 , C_2H_2 , H_2 and CO_2) accounting for 6% of starting ester and liquids accounting for 14% of the starting ester. The liquid products consisted of a series of terminal olefins, $n\text{-C}_n\text{H}_2\text{CH}=\text{CH}_2$, through $n\text{-C}_{13}\text{H}_{27}\text{CH}=\text{CH}_2$, along with a series of corresponding terminal olefins substituted with an ester group, $\text{CH}_3\text{O}_2\text{C}(\text{CH}_2)_n\text{CH}=\text{CH}_2$, $n=4-12$. The esters were each produced in yields comparable to its corresponding simple terminal olefin cleavage pair. This indicates that the ester group remained intact during the carbon-carbon scission reaction.

Microwave Irradiation of Octadecanol. 1-Octadecanol, 1 g, and pine char, 0.05 g, were irradiated at ca. 50 W for one hour. At ca. 30% conversion, products consist of light gases (ca. 50%), the major component of which is ethylene, and liquids (ca. 50%). The liquid products were composed of a series of terminal olefins and a corresponding series of terminal olefins possessing a terminal hydroxyl group ($\text{C}_3 - \text{C}_{17}$). The hydroxylated hydrocarbon terminal olefins and hydrocarbon terminal olefins were formed in approximately equal yields.

Microwave Irradiation of Cyclododecane. Cyclododecane (damp with water, or dried, by exposure of a solution of hydrocarbon in CH_2Cl_2 to anhydrous MgSO_4), 1 g, and white pine char catalyst, 0.05-0.1 g, were warmed to ca. 100°C to melt the waxy hydrocarbon after which irradiation (ca. 50 W) was carried out for 20 min. Dry cyclododecane underwent ca. 21% conversion in 10 min, yielding gaseous products (11%) and liquid products (10%). The liquid products include ring contraction products (22%), acyclic terminal olefins (56%), and acyclic diterminal olefins (14%). The gaseous products contained hydrogen (16%), methane(4%), ethylene (48%), ethane(2%), acetylene (12%), propylene(8%), butene(3%) and butadiene(7%). Damp cyclododecane gave cyclododecanol (19%) and cyclododecanone (26%) as major products, in addition to hydrocarbon products. In the absence of moisture, the products were as follows: **C_{12} Products:** 1-dodecene (14%); **C_{10} Products:** Cyclodecane (21%), 1-methyl-2-propylcyclohexane (2%), n-butylcyclohexane (4%), 1-decene (10%) and 1,9- decadiene(1%); **C_8 Products:** 1-nonene (4.6%), 1,8-nonadiene; **C_6 Products:** Cyclooctane (19.5%), 1-octene(7.5%), 1,7-octadiene (2%); **C_4 Products:** 1-heptene(3%), 1,6-heptadiene (1.6%); **C_2 Products,** cyclohexane (2%).

RESULTS AND DISCUSSION

Ambient Temperature Conversion of Linear Hydrocarbons. Low power microwave irradiation of liquid hydrocarbons in the presence of a catalyst, activated wood charcoal, leads to the remarkably selective production of α -olefins. In the case of hexadecane, conversion up to ca. 30% leads only to α -olefins and light gases, mainly ethylene. Above 30% conversion, the formation of diterminal diolefins becomes significant, and further conversion of lighter olefins to ethylene occurs. Ultimately, ethylene is the major product from hydrocarbons, with small yields of acetylene from further conversion of ethylene and butadiene. The terminally unsaturated hydrocarbons, $\text{C}_3\text{-C}_{13}$, formed from hexadecane are shown in Fig. 1 and Table 1. The gaseous products gave a 47% yield while the liquid products showed a 10% yield, see Table 1. The most notable features of the reaction include (1) the formation of α -olefins from linear alkanes with only trace levels of hydrocarbons, (2) the absence of internal (non-terminal) olefins, and (3) the

REFERENCES

1. Department of Chemistry, University of Alberta, Edmonton, Alberta.
2. Pacific Northwest National Laboratory, Richland, WA.
3. (a) Dayani, R. "Molecular Magic With Microwaves," *Chem. Eng. News*, **1997**, Feb. 10th, 26.
(b) von Hippel, A.R. "Dielectric Materials and Applications," MIT Press, Cambridge, MA., USA **1954**.
(c) Gabriel, C.; Gabriel, S.; Grant, E.H.; Halstead, B.S.J.; Mingos, D.M.P. Dielectric Parameters Relevant to Microwave Dielectric Heating," *Chemical Society Reviews*, **1998**, *27*, 213.
(d) Majetich, G.; Wheless, K. "Microwave-Enhanced Chemistry," *American Chemical Soc. Publication*, H.M. Kingston and S.J. Haswell, Eds. **1997**, Chapter 8.
4. (a) Beeri, A.; Berman, E.; Vishkausan, R.; Mazur, Y. *J. Am. Chem. Soc.*, **1986**, *108*, 6413.
(b) Tanner, D.D.; Zhang, L. *J. Am. Chem. Soc.*, **1994**, *116*, 6683.
(c) Tanner, D.D.; Kandananarachi, P.; Das, N.C.; Brausen, M.; Vo, C.T.; Camaioni, D.M.; Franz, J.A. *J. Org. Chem.*, **1998**, *63*, 4587.
(d) Tanner, D.D.; Zhang, L.; Kandananarachi, P. *J. Phys. Chem.*, **1996**, *100*, 11319.
5. Mingos, D.M.P.; Whittaker, A.G. *J. Chem. Soc., Dalton Trans.*, **1992**, 2751.
6. For examples of Microwave activated catalysis, see
 - (a) A. Revella; Murphy, W.J.; Achia, Biddanda V. "Conversion of C₂+ Hydrocarbons Using Microwave Irradiation", U.S. Pat. 4,975,164 (1990).
 - (b) J.K.S. Wan, "Microwave Induced Catalytic Conversion of Methane to Ethylene and Hydrogen", U.S. Pat. 4,574,038 (1986).
 - (c) J.K.S. Wan, U.S. "Microwave Production of C₂ Hydrocarbons Using a Carbon Catalyst", Pat. 5,472,581 (1995).
 - (d) W.J. Murphy, "Conversion of Methane Using Pulsed Microwave Radiation", U.S. Pat. 5,205,912 (1993).
 - (e) W.J. Murphy, "Conversion of Hydrocarbons Using Microwave Radiation", U.S. Pat. 5,277,773 (1994).
 - (f) W.J. Murphy, D.H. Shaw, "Upgrading of Low Value Hydrocarbons Using A Hydrogen Donor and Microwave Radiation" U.S. Pat 5,181,998 (1993) and U.S. Pat. 5,328,577 (1994).

Product	% Yield (Mole basis)
Liquid Products*, 100-minute reaction	
n-C ₂ H ₅ CH=CH ₂	0.59
n-C ₃ H ₇ CH=CH ₂	1.22
n-C ₄ H ₉ CH=CH ₂	1.24
n-C ₅ H ₁₁ CH=CH ₂	3.23
n-C ₆ H ₁₃ CH=CH ₂	14.7
n-C ₇ H ₁₅ CH=CH ₂	17.6
n-C ₈ H ₁₇ CH=CH ₂	14.8
n-C ₉ H ₁₉ CH=CH ₂	13.4
n-C ₁₀ H ₂₁ CH=CH ₂	13.2
n-C ₁₁ H ₂₃ CH=CH ₂	13.6
n-C ₁₂ H ₂₅ CH=CH ₂	6.27
Gaseous Products*	
H ₂	12.0
CH ₄	4.83
C ₂ H ₄	40.9
C ₂ H ₆	2.05
C ₃ H ₂	7.12
C ₃ H ₆	16.5
CH ₂ CH=CH=CH ₂	8.16
CH ₂ =CHCH=CH ₂	5.76
Others	2.17

*Products normalized to 100%. **Products normalized to 100%

Table 1. Products from Microwave Irradiation of Hexadecane in the Presence of Wood Char.

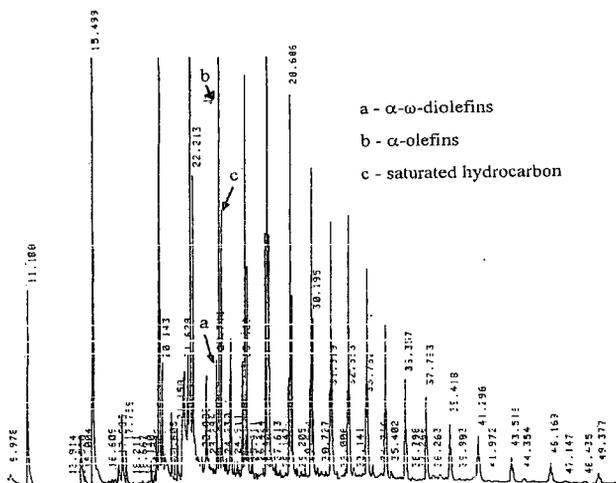


Figure 3. Products Formed from the Catalytic Microwave Oxidative Fragmentation of Polyethylene.

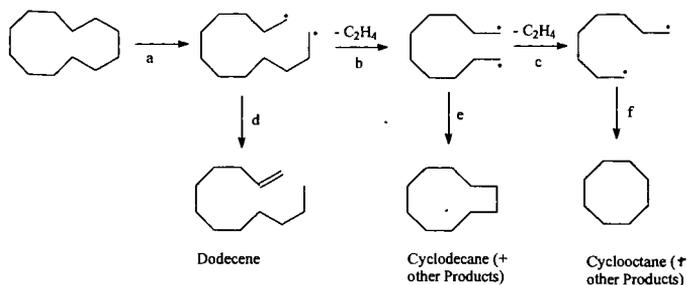


Figure 4. Biradical Mechanism for Hydrocarbon Conversion. Biradical Formation (a) followed by sequential ethylene loss (b,c) with product formation by disproportionation (d) or ring closure (e,f).

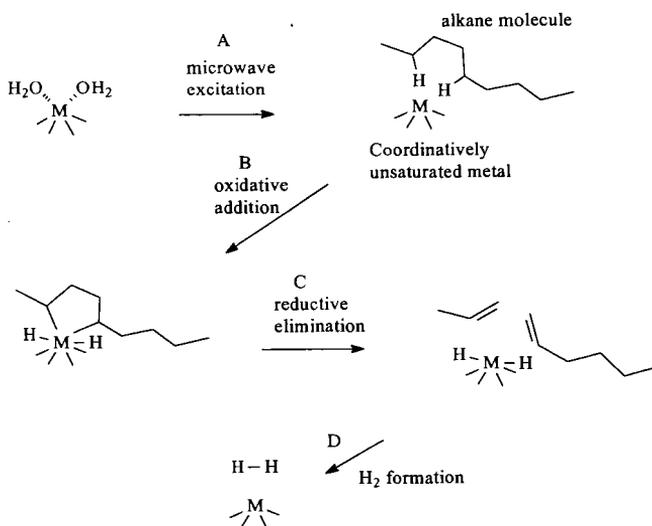


Figure 5. Metal-Centered Catalysis Mechanism for Oxidative Fragmentation of Alkanes.