

MECHANISMS OF
HYDROCARBON REACTIONS
A SYMPOSIUM

5—7 JUNE 1973, SIÓFOK, HUNGARY

Edited by
PROF. F. MÁRTA and DR. D. KALLÓ

AKADÉMIAI KIADÓ, BUDAPEST 1975

The symposium was organized by the Institute
of Isotopes of the Hungarian Academy of Sciences
and
the Society of Hungarian Chemists

President of the Symposium

P. TÉTÉNYI

Honorary President

G. SCHAY

Organizing Committee

Chairman: G. FÖLDIÁK

Secretary: L. GUCZI

Paper Selecting Committee

Chairman: Z.G. SZABÓ

Secretary: Z. PAÁL

Publication Committee

Chairman: F. MÁRTA

Secretary: D. KALLÓ

100 B 225/75

ISBN 963 05 0309 3

© Akadémiai Kiadó, Budapest, 1975

Joint edition published by Akadémiai Kiadó, The Publishing House of the Hungarian Academy of Sciences,
Budapest, Hungary, and Elsevier Scientific Publishing Company, Amsterdam, The Netherlands

PRINTED IN HUNGARY

CONTENTS

TÉTÉNYI, P.: Opening address	11
List of Participants	13

Part One

Heterogeneous Catalytic Reactions

KAZANSKII, B.A.: On the mechanism of hydrocarbon conversions in the presence of some heterogeneous catalysts Plenary lecture 1	15
Obituary: Boris Alexandrovich Kazanskii	47

Catalysis by metals

BOND, G.C.: An extension of the "active centre" concept in hydrocarbon reactions on metal catalysts Plenary lecture 2	49
LUNIN, V.V., LISISHKIN, G.V., BONDAREV, Y.M., DENISOV, L.K.: Mechanism of activation of hydrogen in conversions of hydrocarbons by transition metals of Groups IV-VI Paper 18	71
LEVITSKII, I.I., MINACHEV, Kh.M.: Dependence of the direction of hydrocarbon hydrogenolysis and dehydrocyclization on electron density distribution in catalysts and reacting molecules Paper 15	81
RABINOVICH, G.L., MASLYANSKY, G.N., TREIGER, L.N.: On the reaction mechanism of water steam alkyl-benzene dealkylation on the Group VIII metals Paper 48	97
GRYAZNOV, V.M., PAVLOVA, L.F., KHLEBNIKOV, V.B.: A study of concentrations of surface reagents with the help of membrane catalyst Paper 16	107
RÁCZ, G., SZÉKELY, G., SZÉKELY, É.: Oxidation of o-xylene in a catalyst lined tube reactor Paper 47	117
MINK, Gy., MÓGER, D., NAGY, F.: Hydrogenation of ethylene on platinized platinum Paper 39	125
PAÁL, Z., FRYER, J.R., THOMSON, S.J.: Formation of carbonaceous deposits on platinum black catalysts Paper 31	137

LIETZ,G., VÖLTER,J.: Catalytic hydrogenation of methylbenzenes on platinum Paper 34	151
KOSLOV,N.S., POLIKARPOV,V.A., SENKOV,G.M.: Chemical transformations of the hydrocarbons with alumo-platinum catalysts promoted by the rare earths Paper 23	163
GUCZI,L., KÁLMÁN,J., SÁRKÁNY,A.: On the hydrogenolysis of n-hexane over nickel powder catalysts Paper 20	173
LESZCZYNSKI,A., FRACKIEWICZ,A., PALCZEWSKA,W.: The influence of presorbed hydrogen on ethylene hydrogenation over Ni and Ni-Cu alloy films Paper 8	187
ROSS,J.R.H., STEEL,M.C.F., ZEINI-ISFAHANI,A.: The steam reforming of methane over nickel catalysts Paper 22	201
TOUROUDE,R., GAULT,F.G.: Mechanisms of isomerization and exchange of olefins on iron catalysts Paper 50	215

Catalysis by metal oxides

KRAUSS,H.L.: Reactions of unsaturated hydrocarbons with metal ions on surfaces Paper 36	227
OTREMBAM., TANIEWSKI,M.: The mechanism of transformations of hydrocarbon in the presence of molybdenum oxide on alumina Paper 2	235
GIORDANO,N., VAGHI,A., BART,J.C.J., CASTELLAN,A.: Nature of active sites and mechanism of the heterogeneous interaction of propylene with a $\text{MoO}_3\text{-Al}_2\text{O}_3$ catalyst Paper 55	245
GRZYBOWSKA,B., GERMAN,K., HABER,J., KOWALSKI,T., MAZURKIEWICZ,A.: Active centres in selective oxidation of olefins on molybdate catalysts Paper 54	265
SCHULZ,I.W., SCHEVE,J.: NH_3 oxidation as a model reaction for selective hydrocarbon oxidation Paper 26	283
WISE,H.: Catalytic oxidation and ammoxidation of propylene Paper 25	297
BOZSÓ,F., SOLYMOSI,F.: Oxidation of ethylene, ethylene oxide and propylene on $\text{SnO}_2\text{-Cr}_2\text{O}_3$ catalysts Paper 6	311

Catalysis on insulators

- MÁNDY, T., SCHAY, Z.: Study on the mechanism of the isomerization in olefins on pure aluminas 321
Paper 40
- KNÖZINGER, H., CORADO, A., GÁTI, Gy., HIERSTETTER, H., KISS, Á., LETTERER, R.: Double bond isomerization and D₂-exchange of olefins on alumina 333
Paper 1
- PLATÉ, A.F., ERIVANSKAYA, L.A., HALIMA-MANSOUR, A., SHEVTSOVA, G.A.: Carbonium-ion mechanism of dehydrocyclization of alkenyl-naphthalenes over "acidic" alumina catalysts 345
Paper 17
- GRABOWSKI, W., MALINOWSKI, St.: Isobutane reactions in the presence of ionic surfaces 357
Paper 10

Catalysis by zeolites

- BEYER, H., DETREKŐY, E., KALLÓ, D., PAPP, J.: Dehydroxylation and catalytic activity of some H-zeolites 369
Paper 35
- ZULFUGAROV, Z.G., ZULFUGAROVA, L.Sh., KAHRAMANOVA, Ch.G., MURADOVA, S.A., ANNAGIEV, M.Sh., ASKEROV, A.G., DZHAFAROVA, E.M., DZHAFAROVA, S., YUSIFOVA, Sh.A.: The effect of high-temperature water vapour on the change of the character of surface properties of zeolite catalysts 379
Paper 5
- GRYAZNOVA, Z.V., ERMILOVA, M.M., BASKUNJAN, K.A.: About the mechanism of butene isomerization on zeolite catalysts 389
Paper 19
- LAPIDUS, A.L., ISAKOV, Ya.I., RUDAKOVA, L.N., MINACHEV, Kh.M., EIDUS, Ya.T.: Catalytic oligomerization of i-butene on zeolites 403
Paper 60
- KARGE, H.G.: Alkylation of benzene and polymerization of ethylene with mordenite as catalyst 417
Paper 53
- BREMNER, H., WENDLANDT, K.P.: Isomerization and disproportionation of methylaromatics on zeolite catalysts 431
Paper 38
- DOROGOCHINSKY, A.Z., HADZHIEV, S.N., GAIRBEKOVA, S.M.: Regularities in the changing of the activity and selectivity of zeolite type-Y with the different chemical composition in gas oil cracking 443
Paper 49

- ÓRHALMI, O., FEJES, P.: Heterogeneous catalytic transformations of propylene on a Y-type decationised molecular sieve catalyst
Paper 11 457
- ARESHIDZE, Kh. I., LAPIDUS, A. L., DOLIDZE, A. V., EIDUS, Ya, T.: Catalytic transformation of alkenyl- and alkylidene-cyclobutanes in the presence of silica-alumina catalysts
Paper 14 469

Part Two
Homogeneous Reactions
Catalysis by Coordination Compounds

- SHILOV, A. E., SHTEINMAN, A. A.: H-D exchange and other reactions of saturated hydrocarbons in solutions of transition metal complexes
Paper 13 479
- ZAKHAROV, V. A., BUKATOV, G. D., DEMIN, E. A., YERMAKOV, Yu. I.: Coordination mechanism of insertion reactions into metal-carbon bond at catalytic polymerization of olefins
Paper 28 487
- STEFANOVSKAYA, N. N., SHMONINA, V. L., TINYAKOVA, E. I., DOLGOPLOSK, B. A.: The nature of active centres and stereospecificity in diene polymerization under the influence of π -allyl complexes of chromium
Paper 45 497
- BELOV, G. P., DZHABIEV, T. S., D'YACHKOVSKIY, F. S.: Catalytic dimerization of ethylene in 1-butene
Paper 4 507
- SIMON, Á., CSIZ, L., MARKÓ, L.: Kinetics and mechanism of the homogeneous alkylbenzene disproportionation
Paper 33 517
- KORSHAK, Yu. V., VARDANYAN, L. M., DOLGOPLOSK, B. A.: Catalytic disproportionation of cyclo-olefins by $\text{Al}(\text{iso-C}_2\text{H}_5)_2\text{Cl-WCl}_6$ system
Paper 46 527

Pyrolysis

- SERES, L., AUSLOOS, P.: On the mechanism of the thermal decomposition of propylene
Paper 37 539
- ZALOTAI, L., BÉRCES, T., MÁRTA, F.: The role of olefinic products in the pyrolysis of propane
Paper 43 551

BRADLEY, J.N.: The high temperature pyrolysis of isobutane Paper 7	565
GÖRGÉNYI, M., SERES, L., MÁRTA, F.: The effect of nitric oxide on the thermal decomposition of isobutane Paper 42	577
ROSSKAMP, G., SUHR, H.: Cyclobutadiene: a probable intermediate in hydrocarbon polymerization at high temperature Paper 51	587
SCACCHI, G., LARGE, J.F., MARTIN, R., NICLAUSE, M.: The acceleration or inhibition of oxygen during pyrolysis of some alkanes at about 500 °C Paper 12	593

Radiolysis

AUSLOOS, P.: Pulse radiolysis of alkanes in the gas-phase, ion-molecule reactions and neutralization mechanism of hydrocarbon ions Plenary lecture 3	603
SANTAR, I.: Primary yields in hydrocarbons: basic information for understanding the radiolytic mechanisms Paper 56	625
TILQUIN, B., ALLAERT, J., CLAES, P.: Dissolution method for free radical capture in the radiolysis of solid hydrocarbons Paper 9	639
GÄUMANN, T., RUF, A.: The hydrogen evolution in saturated hydrocarbons Paper 44	647
FÖLDIÁK, G., CSERÉP, Gy., HORVÁTH, Zs., WOJNÁROVITS, L.: The influence of cyclic structure on the radiolysis of hydrocarbons Paper 41	659
RODER, M.: On the radiolysis of the cyclohexane-hexamethylbenzene mixtures Paper 59	675
PODKHALYUZIN, A.T., VIKULIN, V.V., VERESHCHINSKII, I.V.: Radiation-chemical alkylation with adamantane Paper 58	687
BARTONICEK, B., HLADKY, E., SCHWEINER, Z., BEDNÁR, J.: Study of radiation formation of methyl-iodide. II. Chain decomposition of methane-iodine mixtures at elevated temperatures Paper 57	695

Oxidation

- NEMES, I., DANÓCZY, É., VIDÓCZY, T., VASVÁRI, G., GÁL, D.: 703
Problems in liquid phase hydrocarbon oxidation
Paper 52
- RAY, D.J.M., WADDINGTON, D.J.: Gas-phase oxidation of 721
2,2-dimethylpropane
Paper 29
- IRVINE, G.W., KNOX, J.H.: The role of surface in com- 733
petitive oxidation of alkanes between 300 and 480 °C
Paper 32
- BROWN, A.J., BURT, N.H., LUCKETT, C.A., POLLARD, R.T.: Thermo- 751
kinetic studies of the cool-flame and multi-stage igni-
tion of hydrocarbons
Paper 21
- BASTOW, A.W., CULLIS, C.F.: The influence of hydrogen 765
bromide on the combustion of hydrocarbons
Paper 3

General

- GOLDSTEIN, M.J., BENZON, M.S., HAIBY, W.A., JUDSON, H.A.: The 779
Linear Analysis of Labeling Experiments (LALÉ)
Plenary lecture 4
- Author Index 811

Opening address by P.Tétényi

It is a great honour and a great pleasure to me to greet you on behalf of the organizing bodies of our Symposium, namely the Hungarian Academy of Sciences, the Institute of Isotopes and the Society of Hungarian Chemists. I am very pleased that you have accepted the invitation to attend our scientific meeting in such a great number.

The investigation of the chemistry and transformation of hydrocarbons has an increasing importance in chemical research. The development and improvement of the experimental methods give more and more possibilities for a thorough study of hydrocarbons which do not possess characteristic functional group in their molecules, enabling us to increase our knowledge about their behaviour under different experimental conditions.

The chemical transformations of hydrocarbons play an important role in chemical industries, too. They are important not only as energy resources but as starting materials for chemical industries all over the world. This latter role is increasing also due to the appearance of new energy sources giving, thus, more possibilities to use hydrocarbons for other chemical purposes. Consequently, more attention will be focused by different research institutions and groups on the chemical transformation of hydrocarbons.

This was our impression at the Fifth Congress of Catalysis in Palm Beach last year, when about 40% of the lectures dealt with catalytic transformation of different hydrocarbons. Advanced research works which are in progress for example at the Universities of Moscow, Princeton, Stanford and Berkeley, in the Zelinskii Institute of Organic Chemistry of the Soviet Academy of Sciences as well as in the Institute of Catalytic Research in Lyon all show that catalytic research and hydrocarbon chemistry have merged to a great extent.

In addition, present radiation sources of very high intensity and improved analytical methods are available and this is the reason why radiation research also turns more and more towards the study of hydrocarbon reactions.

In Hungary wide-spread work has started on utilizing the chemical transformation of hydrocarbons in the petroleum industry. This has created a demand to widen the research in the field of hydrocarbon chemistry. I feel that this is one of the main reasons to have organized this scientific symposium here and now. It seems to me that it would be very interesting and fruitful if scientists who are dealing with the different ways of the initiation of hydrocarbon reactions, such as by heterogeneous and homogeneous catalysts, by irradiation and thermal energy come together to discuss these problems, bearing in mind that the main aim is to obtain as much information as possible on the mechanisms of the hydrocarbon reactions. The synthesis of the different ways of initiation may give a deeper insight into the explanation of any given reaction mechanism.

More than fifty contributed papers and four plenary lectures will be delivered during the Symposium and the members of the Symposium have come from twelve countries. It is my pleasant duty to thank all those concerned for their valuable contributions.

A few weeks ago we received the sad message from Russia that Professor Kazanskii, member of the Soviet and many other Academies of Sciences, one of the initiators of catalytic hydrocarbon chemistry had died on 5th April at the age of 82. We wish to convey our deepest regrets and sympathy to his co-workers and all our Soviet colleagues. May I suggest that we honour his memory with a 1 minute silence.

His colleagues completed the plenary lecture drafted by Professor Kazanskii himself. It will be delivered by one of his closest co-workers, Professor Rozengart.

I would like to express my gratitude to the bodies organizing the Symposium as well as the Ministry of Heavy Industry for their financial support.

And now, I would like to ask Professor Schay, honorary chairman of our symposium, the Great Old Man of Hungarian physical chemistry to say some words of welcome to the participants.

LIST OF PARTICIPANTS

Belgium	Bérces, T.	Péter, A. (Miss)
Claes, A.M. (Mrs)	Beyer, H.	Rácz, Gy.
Claes, P.	Bozsó, F.	Raskó, J.
Tilquin, B.	Cserép, Gy.	Róder, M.
	Csiz, L.	Rózsa, M. (Miss)
CSSR	Czárán, E. (Mrs)	Sárkány, A.
Hetflejš, J.	Danóczy, É. (Mrs)	Schay, G.
Hofman, J.	Detrekőy, E.	Schay, Z.
Krivánek, M.	Dobrovolszky, M. (Mrs)	Schiller, R.
Santar, I.	Engelhardt, J.	Seres, I.
Schweiner, Z.	Farkas, L.	Seres, L.
	Fejes, P.	Simándi, L.
France	Földiák, G.	Simon, A.
Gault, F.G.	Fölkl, P.	Siska, J.
Large, J.F.	Gál, D.	Solymosi, F.
Lucquin, M.	Gáti, Gy.	Steingaszner, P.
Martin, R.	Gedra, A. (Miss)	Stenger, V.
Niclause, M.	Görgényi, M.	Szabó, S.
Scacchi, G.	Guczi, L.	Szabó, S. (Mrs)
	György, I.	Szabó, Z.G.
GDR	Hartwig, I.	Szakács, S.
Bremer, H.	Herendi, J.	Szepesváry, É. (Mrs)
Bremer, U. (Mrs)	Hollai, M. (Mrs)	Szepesváry, P.
Graefe, J.	Horváth, Zs. (Miss)	Szepesy, L.
Glietsch, J.	Huhn, P.	Tétényi, P.
Hoffman, J.	Illés, V.	Vajta, L.
Lietz, G.	Izsák, Gy.	Vasvári, G.
Ritschl, F.	Kalló, D.	Vidóczy, T.
Schulz, I.W.	Kálmán, J.	Votisky, L.
Völter, J.	Király, J.	Weisz, I.
Wendlandt, K.P.	König, P.	Wojnárovits, L.
Zimmermann, G.	Kőrös, E.	Zalotai, L.
	Kovács, A.	
	Kovács, G. (Mrs)	
	Kuty, H. (Mrs)	
	Magyar, M.	Italy
GFR	Markó, L.	Giordano, N.
Christoffel, E.	Mándy, T.	
Höhlein, B.	Margitfalvi, J.	Netherlands
Knözinger, H.	Márta, F.	Sachtler, W.
Knözinger, R. (Mrs)	Matusek, K.	
Roskamp, G.	Mezei, M. (Mrs)	Poland
Vierrath, H.	Mink, Gy.	Berak, J.
	Móger, D.	Grzybowska-
Hungary	Nagy, F.	-Swierkosz, B. (Mrs)
Ács, G.	Naszódi, L.	Haber, H. (Mrs)
Babernits, L.	Németh, A.	Haber, J.
Bakos, M.	Órhalmi, O. (Miss)	Leszczynski, A.
Báthory, J.	Paál, Z.	Malinowski, St.
	Petró, J.	

Otremba, M.
Palczewska, W.
Sloczynski, J.
Taniewski, M.
Zatorski, L.
Zatorska, W. (Mrs)

Switzerland

Gäumann, T.

United Kingdom

Bond, G.C.
Bradley, J.N.
Burt, N.
Pollard, R.T.
Ray, D.J.M.
Ross, J.

USA

Ausloos, P.
Goldstein, M.J.
Sieg, R.
Sieg, V. (Mrs)
Wise, H.
Wise, T. (Mrs)

USSR

Akhmedov, V.M.
Areshidze, Kh.I.
Belov, G.P.
Davidov,
Dolidze, A.V.
Ermilova, M.M.
Gryaznov, V.M.
Gryaznova, Z.V.
Hadzhiev, S.N.
Korshak, Yu.V.
Koslov, N.S.
Krivorutsko,
Lapidus, A.L.
Levitskii, I.I.
Lunin, V.V.

Markevich, S.
Platé, A.
Rabinovich, G.L.
Rozengart, M.J.
Shebaldova, A.D. (Mrs)
Stefanovskaya, N.N.
Shteinman, A.A.
Vereshchinskii, I.V.
Zakumbayeva, C.D.
Zakharov, V.A.
Zulfugarov, Z.G.

West Berlin

Horváth, B.
Horváth, É. (Mrs)
Karge, H.G.
Krauss, H.L.
Krauss, M. (Mrs)