CATALYTIC REACTIONS AT HIGH PRESSURES AND TEMPERATURES

by

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FOREWORD

This book primarily is a collection and review of my researches in the field of catalysis during the past thirty-five years. The task of writing it was undertaken because I believed that a collection of these researches would be of interest and much of my published work is otherwise inaccessible.

This book is my chemical autobiography. For that reason, no attempt was made to collect the literature or to include the work of others except in special cases where it was desirable to emphasize and develop certain features, or where it was considered to have a direct bearing upon my own researches.

I have devoted my entire scientific lifetime to the exploration of this little known and difficult field. In the interests of the history of catalysis, it is important that the correct significance be placed upon my investigations.

This has not always been done. A number of authors of monographs on catalysis have not referred at all to my original publications. However, Marek in his book, "The Catalytic Oxidation of Organic Compounds in the Vapor Phase" (1932) placed the true value upon my investigations of the catalytic decomposition of alcohols under the influence of specific catalysts.

In some cases, my work has been criticized. For instance, one specialist in catalysis wrote: "The application of the expensive and dangerous apparatus in not compensated by the advantages of the Ipatieff method."

Today, all workers in catalysis realize the importance of high pressure. The dangers incident to its use have been greatly exaggerated. My co-workers and I, since 1903, have safely made several thousand high pressure experiments in bombs of my own design. My method of bomb closure has been widely adopted.

Only by application of high pressure is it possible to hydrogenate completely and obtain pure products (free from traces of starting material). At the present time, cyclohexane, tetralin, decalin, and numerous other products are produced commercially by my high pressure methods.

I was the first to demonstrate the possibility of hydrogenating in the liquid phase (the hydrogenation of liquid hydrocarbons and of the salts of unsaturated acids). These results would be impossible according to the theory and method of Sabatier.

The above title was given to the book since the dominant feature is pressure and I am the pioneer in the use of pressure in chemical reactions. However, many reactions are described which were made at ordinary pressure.

My investigations during the past five years have resulted in the development of certain hypotheses applicable to the catalytic reactions of dehydration, polymerization, alkylation, and isomerization. Some of these results are published for the first time in this book.

The reader will find numerous studies which I did not finish because of the conditions under which I worked. These unsolved problems have not lost their interest and I shall feel fully compensated for this publication if it inspires others to further work in this field.

未解决

I wish to express my deep gratitude to my beloved wife, Barbara, to my life-long friend Professor Willstaetter, to Mr. Hiram Halle and the Universal Oil Products Company for material support, to Drs. Gustav Egloff, A. v. Grosse, and Jacques Morrell for helpful suggestions, and to Drs. S. Berkman, B. B. Corson, and R. E. Schaad for translating and correcting the book.

建议

翻译

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By Professor R. Willstaetter (München)

Die Jugendarbeiten von Ipatieff wurzeln in den grossen Traditionen der russischen Chemiker. Sie liefern schöne Beiträge zur Kenntnis der Kohlenwasserstoffe, insbesondere der Additionsreaktionen ungesättigter Kohlenwasserstoffe. Schon hier, namentlich in den Untersuchungen über die Konstitution und die Synthese des Isoprens vom Jahre 1897 tritt die Selbständigkeit und Originalität in der Wahl und Behandlung grosser Probleme hervor, die Jahrzehnte später in der Entwicklung der organischen Chemie eine Rolle spielten.

In noch höherem Masse gilt dies für die aus sehr zahlreichen und gründlichen Untersuchungen bestehende Hauptgruppe des Lebenswerkes von Ipatieff, dass darin neue Probleme, neue Wege, neue Methoden eröffnet werden und zwar von solcher Tragweite, dass darin die moderne Entwicklung der anorganischen und organschen technischen Chemie vorgeahnt und angebahnt erscheint. Die Arbeiten von Ipatieff über "Pyrogenetische Kontaktreaktionen organischer Verbindungen" und über "Katalytische Hydrierungen" sind nämlich durch zwei Umstände ausgezeichnet: durch Einführung sehr hoher Drucke und durch die Wahl und Variationen der Katalysatoren.

Heute wird als eine Hauptaufgabe der Chemie die Erforschung des Wesens, der Wirkungsweise und die Konstitution der organischen Katalysatoren, der Fermente, deutlich. Und in der praktischen Chemie hat die Ausgestaltung der Lehre von den anorganischen Katalysatoren, die Steigerung ihres Leistungsvermögens und ihre Ausbildung für spezifische Reaktionslenkungen in den technischen Methoden der Ammoniaksynthese, der Salpetersäuregewinnung, der Hydrierung von Kohlenoxyd, der Gewinnung von Benzinen aus Kohle, ihre überragende Bedeutung erwiesen. Der zweite wesentliche Umstand in den Arbeiten von Ipatieff über Katalyse und zwar schon in den ersten Jahren dieses Jahrhunderts war die Anwendung sehr hoher Drucke. Dieses Prinzip ist in den letzten zwei Jahrzehnten seit dem Erfolg der Haber'schen Ammoniaksynthese immer mehr zu einer beherrschenden Methode für grossindustrielle Prozesse geworden.

Diese neue Prinzipien sind in den Untersuchungen von Ipatieff ausserordentlich früh angewandt worden. Ipatieff zählt daher zu den grossen Anregern und Förderern der Chemie unserer Zeit.

TRANSLATION

Ipatieff's early work is rooted in the great traditions of the Russian chemists. He made excellent contributions to the knowledge of hydrocarbons, especially of the addition reactions of unsaturated hydrocarbons. Independence and originality in the choice and treatment of broad research problems, which decades later were to play a part in the development of organic chemistry, were apparent in his early work on the constitution and synthesis of isopropene in 1897.

Indeed, independence and originality are manifest throughout the many fundamental investigations in the field which was his life work. His problems and his methods of attack seem to foreshadow and to prepare the way for the modern developments of organic and inorganic industrial chemistry. The works of Ipatieff on "Pyrogenetic Contact Reactions of Organic Compounds" and "Catalytic Hydrogenation" are distinguished by two particular features: the choice and variety of catalysts and the introduction of very high pressures.

Today one of the major problems of chemistry is the investigation of the nature, the mode of reaction, and the structure of the organic catalysts, the ferments. Of great importance in applied chemistry is the study of inorganic catalysts, increasing their effectiveness and developing suitable catalysts for specific reactions such as the synthesis of ammonia, the manufacture of nitric acid, the hydrogenation of carbon monoxide, and the production of liquid fuels from coal. The second important feature of Ipatieff's study of catalysis, applied in the first years of the century, was the use of very high pressures. In the last two decades, since the success of the Haber ammonia synthesis, high pressures have become increasingly important in industrial processes.

These new principles were used very early in Ipatieff's investigations. Ipatieff, therefore, is one of the great pioneers in the chemistry of our day.

INTRODUCTION

At the beginning of the 20th century very little study from the chemical viewpoint had been given to pyrogenetic reactions of decomposition of organic compounds.

In spite of the fact that the dry distillation of organic compounds was so important in the production of many substances, pyrogenetic reactions had not been investigated with the completeness necessary for clarification of their course when yielding various products. Probably the variety of products obtained was the chief reason that pyrogenetic processes did not receive more scientific investigation.

Almost all investigators held a definite opinion that at high temperatures (above 300–400°) the molecules of an organic compound would decompose in various, probably selective directions, and that the resulting fragments of molecules would combine with each other to form various compounds. In such pyrogenetic processes different reactions of decomposition, polymerization, and condensation could be observed, and their sequence followed. To explain the formation of this or that product seemed to be a very difficult matter, and in some cases even impossible. It should be noticed that investigators of pyrogenetic reactions paid very little attention to the temperature at which the process occurred and nobody attached much significance to the material of the vessel in which the pyrolysis was conducted. After making numerous investigations on organic substances at high temperatures and pressures during the first third of the 20th century, it became obvious to us why pyrogenetic processes could not attract the minds of chemists. Primarily a study of the pyrolysis of the simplest organic compounds was necessary and observations had to be made of the laws of their decomposition and the course of other concurrent reactions that can take place.

The first significant investigation of pyrogenetic reactions was made by Berthelot, who showed in a series of works the most interesting pyrogenetic syntheses of various hydrocarbons. But in the pyrogenetic reactions studied by Berthelot as well as by others, the main effect was ascribed to the temperature (thus these reactions were named pyrogenetic) and no attention at all was paid to many other conditions of the experiments.

Thus, for example, indications are found in the literature that even before the time of Berthelot ethyl alcohol had been subjected to pyrogenetic decomposition by passing it through a glowing tube. Different writers stated that they had used tubes made of various materials: glass, porcelain, glass containing pumice, etc., but no one attached significance to the latter circumstance, nor accurately measured the temperature at which the process was conducted. Therefore, it is understandable why the various writers obtained different results. Deyman in describing the decomposition of ethyl alcohol in a glass tube indicated that a gas was formed which burned with a weakly luminous flame. Marchand obtained carbon, aldehydes, and gas by leading vapors of ethyl alcohol through a glowing porcelain tube packed with pieces of pumice. Sassure obtained aldehyde among the products of decomposition of ethyl alcohol. At the end of the 18th century, four Dutch chemists, Deyman, Van Trooswyk, Lauwrenberg, and Bondt observed the decomposition of ethyl alcohol by kaolin into gases in which ethylene predominated. Finally Thiele in 1898, in studying the pyrogenetic decomposition of isoamyl alcohol with the object of obtaining butadiene, employed an iron tube merely for the safety of the experiment.

However, in spite of the variety of results obtained by the decomposition of one of the simplest organic substances under the influence of high temperature, nobody was interested in finding the real reason for these variations or in studying quantitatively the products of the reactions.

At this time the frequently used decomposition of alcohols by zinc chloride at a temperature of about 300° was considered as a pyrogenetic reaction, and it was assumed that even at this temperature a complete decomposition of the molecule took place. The fact that various products resulted was considered possible only by the supposition that the molecule of alcohol split into several fragments.

If attention be paid as to how this reaction has been conducted by various writers it is seen that even the temperature of the reaction was not measured accurately, no attention was given to the question of what became of the zinc chloride, and no significance was attached to the walls of the vessel in which these pyrogenetic reactions occurred.

Besides, at that time the decomposition temperatures of organic compounds were not even known approximately, as only the general action of heat had been observed, for example, the behavior of alcohol vapor in a glowing glass tube. Therefore, it is understandable that it was then out of the question to observe the action of catalysts upon the course of the decomposition of carbon compounds at high temperatures.

Actually in order to solve the question as to whether catalysis takes place in the decomposition of organic compounds it is extremely important to know the temperature a certain splitting of the molecule under the influence of heat alone and also the temperature of the same decomposition of the molecule when taking place in presence of certain substances. If the substance introduced strongly decreases the temperature of the decomposition of the organic compounds in a certain direction, and if the substance itself remains unchanged, the latter will be a catalyst and consequently the decomposition reaction will be catalytic.

Up to the beginning of the 20th century no one had succeeded in observing that at high temperatures (above 300°, and especially at 500–600°) a catalyst could influence the course of decomposition of an organic substance and force the decomposition to go in a certain direction only.

In the year 1900, I was the first to answer this question positively in a study of the pyrogenetic decomposition of isoamyl alcohol at 520–540°. The alcohol vapors were passed through an iron tube in order to obtain butadiene and a study was made of the liquid products of decomposition which had not been investigated previously.

The main product of the reaction was isovaleric aldehyde mixed with unreacted alcohol. These data immediately drew my attention to the factor which had not been considered by other investigators as playing any part in the pyrogenetic reactions of organic compounds, namely the material of the vessel in which the decomposition of the organic substance took place which might play the part of a catalyst. From the beginning of my work on pyrogenetic reactions, it was apparent that I was dealing with contact phenomena, because of a certain difference in the products of decomposition of organic substance which had been noticed depending upon the material of the tube in which the pyrogenetic reaction occurred. Also I was able to guide the reaction in a definite direction by correct choice of catalyst. Of course it is not possible to study accurately the decomposition reaction of organic compounds occurring under the influence of heat alone, without the influence of foreign substances, because the walls of the reaction vessel always influence the course of the reaction, although possibly only to a small extent. At the beginning of the investigation of reactions at high temperatures these reactions were divided into two classes: the simple pyrogenetic and the catalytic pyrogenetic; the latter reaction indicated application of catalysts which strongly decrease the temperature of decomposition and force the molecule to decompose in a definite direction with the formation of definite products. During the first two years (1900–1902) I was the first to establish definitely that alcohols might be decomposed in two ways under the influence of catalysts at high temperatures: (1) With the formation of almost pure aldehyde or ketone and hydrogen under the influence of zinc, iron, brass, etc., and oxides of the same metals (zinc oxide, iron oxide, copper oxide, etc.),

$$\begin{gathered}RCH_2OH \rightarrow H_2 + RCOH\\ R{-}CHOH{-}R \rightarrow H_2 + R{-}CO{-}R\end{gathered}$$

and (2) with the formation of ethylene and water only under the influence of alumina and kaolin:

$$RCH_2OH \rightarrow H_2O + C_2H_4$$

In the next year (1903) a third kind of decomposition of ethyl alcohol was discovered by which *butadiene* (divinyl) was formed under the influence of powdered aluminum and alumina.

$$2CH_3CH_2OH \rightarrow 2H_2 + H_2O + CH_2{=}CHCH{=}CH_2$$

When the influence of catalysts upon the course of the decomposition of organic compounds was established with certainty, I gave my attention at once to the necessity of investigating these catalytic reactions in a closed space in order to study them from the viewpoint of chemical kinetics and to solve the question of their reversibility. Besides it was extremely interesting to study the influence of the new factor, pressure, upon the course of catalytic processes.

The study of catalytic reactions at high temperatures and pressures encountered great difficulties at this time (1901–1903) because it was impossible to find an autoclave in Russia or abroad which would permit work at 400–500° under pressure up to 400 atmospheres. The autoclaves of that time made for pressures of 25 to 50 atmospheres could not be used with safety even for such small pressures. By the end of 1903, after a series of attempts, such an apparatus, or a bomb, was constructed. It had such a safe closure that the investigation of a variety of catalytic reactions at high temperatures and pressures could be safely made. In this bomb several thousand experiments were carried out. For laboratory work the closure proposed seems to be the safest and most satisfactory.

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The study of catalytic reactions under pressure at high temperatures immediately gave very valuable results. First it was shown that many catalytic reactions are reversible at high temperatures and that it is possible to observe the intermediate phases of the reaction although such observations are impossible at ordinary pressure. Under pressure the process of hydrogenation proceeds with much greater velocity and it is possible to hydrogenate organic compounds which decompose under ordinary pressure at the necessary temperature. For the first time it was ascertained that hydrogenation proceeds in both liquid and solid phases (hydrogenation of salts), and in aqueous solutions. The introduction of the pressure factor into catalytic reactions at high temperature made hydrogenation possible on a plant scale. Besides this it was possible to investigate many reactions from a kinetic standpoint because of the possibility of following the course of the reaction by pressure readings on the manometer. Thanks to this method for the study of reactions of organic compounds under pressure, it was possible to investigate the effects of temperature, pressure, and catalyst in very important reactions, which were checked later by other workers and operated on a plant scale for obtaining products valuable to the chemical industry. During the period 1903 to 1914, I studied the following reactions under pressure:

(1) Decomposition of organic compounds with and without hydrogen in the presence and absence of catalysts in a bomb with iron walls or in autoclave made of phosphor bronze; (2) Hydro-

genation of various classes of organic compounds in the presence of various catalysts, especially of metal oxides; (3) Dehydration of aliphatic and cyclic alcohols; (4) Isomerization; (5) Polymerization of olefins; (~~6~~) Destructive hydrogenation.

The latter work (6) was carried out in 1926. Because of other work and the Revolution I was forced to discontinue my scientific activity from 1914 to 1922. During the World War, from 1914 to 1917, I was engaged in directing the Chemical Industry in providing munitions, gas, and gas-masks.

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In 1910 while studying the hydrogenation of organic compounds, I noticed a very important fact that hydrogenation occurs especially favorably and at a lower temperature when a certain amount of another substance is added to the catalyst. This substance, often called the promoter, helps the reaction, although it is not able to catalyze the hydrogenation alone. Its help comes through a catalytic side reaction which it produces. It was found possible to explain such reactions by the joint action of catalysts and to predict when substances might be promoters for hydrogenation.[1] However, it was known a long time ago that the addition of certain substances in catalytic reactions accelerates the process, although nothing had been described on hydrogenation processes at high temperatures and pressures either in the literature or in the patents up to 1910. Consequently Prof. Taylor and Prof. Rideal in their book on catalysis ascribe to me the honor of the discovery of the influence of promoters upon the action of catalysts. As is known at the present time, catalytic reactions have to be performed in a great number of cases under the joint action of catalysts.

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At the beginning of the discovery of catalytic reactions in the decomposition of alcohols (1901), I proposed an hypothesis concerning the explanation of these reactions under the influence of metals and their oxides. This hypothesis was discussed superficially by Sabatier and Senderens in the pages of "Comptes Rendus" in 1903, but strange to say, my hypothesis was not even mentioned in Sabatier's book, "La Catalyse dans la Chimie Organique."

First, the hypothesis made possible the prediction of the ways in which metals and their oxides might be good catalysts for the

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[1] This discovery which I made in 1909 and 1910 and published in 1910 in the Ber. Deut. Chem. Ges. drew the attention of Prof. Paal at once, who in the next article in the Berichte D. Ch. G. indicates the importance of this observation and its application in his work on hydrogenation according to this method.

aldehyde decomposition of alcohols. Secondly, this hypothesis also led me to the discovery of alumina as catalyst for dehydration of alcohols, and furthermore, to the discovery of mixed catalysts and the effects of promoters. This hypothesis which led to the prediction of new facts and permitted the simplest explanation of catalytic processes from the chemical viewpoint should merit attention. Also I feel justified in indicating the date of its appearance in science. 证明为正当

加之， Moreover this seems to be warranted because in many monographs[1] as well as in publications by various writers on the theory of catalysis, a definite indication may be found in support of the fact that metal oxides and water play an essential part in catalytic reactions of hydrogenation and dehydrogenation. On the other hand, the works of Langmuir prove that the surfaces of metals are covered by thin oxide films, which according to my hypothesis play an essential part in catalytic reactions.

The same hypothesis led me also to the explanation of the phenomenon of polymerization by the action of various catalysts and the discovery of new catalysts for the alkylation by olefins of a whole series of organic compounds: the paraffin, naphthene, and aromatic hydrocarbons, as well as phenols and other substances.

From 1923 to 1933 when circumstances again favored the continuation of my scientific activities in the laboratory of the Academy of Science and later in the Institute of High Pressure established by me, destructive hydrogenation and condensation under the action of mixed catalysts were studied. More recently my attention was centered chiefly on the study of polymerization of olefins and the alkylation of various classes of organic compounds.[2] This most recent period of my scientific work was facilitated by the coöperation of many associates, and I was therefore able to organize the work on a larger scale than was possible before 1914.

In 1908, I applied high pressure methods to the study of reactions of inorganic compounds. At the beginning of the investigation with aqueous solutions of metallic salts, it was observed that pressure and temperature had an enormous effect upon the course of the reaction. I was the first to succeed in separating

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[1] H. Wolbing, "Hydrierung," 1926, p. 97, Kohle-Koks-Teer, Vol. 8.

[2] Universal Oil Prod. Co., Riverside, Ill.

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metals such as copper, nickel, cobalt, tungsten, lead, cadmium, zinc, etc., from their solutions by means of hydrogen.

Thanks to the investigation of reactions of inorganic compounds under pressure it was possible to separate metallic oxides, double salts, and silicates in excellently formed crystals and to effect the formation of kaolin.

The study of oxidation processes with water under pressure led to the discovery of the oxidation of phosphorus by water with formation of phosphoric acid and pure hydrogen as the final products. The material accumulated in recent times concerning the reactions of inorganic compounds is so large that its systemization and description requires a special monograph which I hope to write in collaboration with my son V. Ipatieff, Jr., who has done much interesting work in this field.

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The study of catalytic reactions in organic chemistry at various temperatures develops more and more, but much more work is still necessary before we can explain the chemical actions of catalysts and be able, by using contemporary physico-chemical methods, to clear up the relationship which exists between the physical and chemical properties of a catalyst and the properties of the substances catalyzed.

The study of catalytic reactions of organic substances at high temperatures and pressures is interesting also because, in all probability, it will lead to the explanation of many processes which occur with organic compounds in the depths of the earth. This concerns also the inorganic compounds. The pressure, temperature, and the character of the substances with which the decomposed organic substance comes in contact must influence the course of its decomposition and consequently various products must be obtained. It is possible that the investigation of catalytic reactions occurring at high temperatures and pressures will give the proper material for the clarification of the question of the origin of petroleum and will offer an explanation of various properties possessed by the different kinds of petroleum found in nature.

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