FORGOTTEN CONTRIBUTION OF V. N. IPATIEFF: PRODUCTION OF BUTADIENE FROM ETHANOL

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Introduction

In 1910, the Russian chemist S. V. Lebedev polymerized butadiene from grain alcohol and obtained a synthetic rubber, which was used in the USSR during and after World War II. In the period of 1928-1931 Lebedev investigated the properties of butadiene rubber using sodium as catalyst, found active fillers for it and suggested the composition of rubber products from synthetic rubber. In 1930, an experimental plant was built in Leningrad, and several hundred kilograms of synthetic rubber were produced in it in 1931.

However, it is known that V. N. Ipatieff began to study the properties of butadiene much earlier, in 1900-1903. At that time, the young researcher prepared an article for the journal of the German Chemical Society and made a report in January 1901 to the Russian Physico-Chemical Society (RPhChS) on pyrogenetic reactions by organic substances.

Lebedev's reaction is widely known, but very few people know about Ipatieff's contribution to the study of this reaction. The authors of the present paper want to help restore recognition to one of the greatest chemists of the 20th century who worked in the field of organic chemistry and who was unfairly forgotten in the course of history.

A historical review on the production of butadiene makes it possible to distinguish some methods for the production of butadiene:

1) Isolation from pyrolysis of amyl alcohol by E. Caventou (1).

2) Production by the steam cracking process used to produce ethylene and other alkenes (2). When aliphatic hydrocarbons are mixed with steam and heated to very high temperatures (above 900 °C) for a short period of time, they undergo dehydrogenation to produce a mixture of unsaturated hydrocarbons, including butadiene.

3) Production by the catalytic dehydrogenation of *n*-butane over Al_2O_3 and Cr_2O_3 at high temperatures (3).

4) Production by catalytic dehydrogenation of *n*-butenes. This method was used in the USA during World War II (4). After World War II, this production pathway from *n*-butenes became the major type of butadiene production in the USSR.

5) Production from ethanol. While not competitive with the second method for production of large volumes of butadiene, lower capital costs make production from ethanol a viable option for smaller-capacity plants. There are two processes in use:

a) Lebedev's conversion of ethanol (5-7) to butadiene, hydrogen and water at 400-450 °C over catalysts in one reactor:

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

b) I. I. Ostromislensky working at Russia's main rubber company Bogatyr (Богатырь) in 1915 proposed a conversion method (8, 9) which is dehydrogenation of ethanol over alumina or clay catalysts to acetaldehyde in the first reactor and then conversation of a mixture of ethanol and acetaldehyde to butadiene over a tantalum-promoted porous silica catalyst in the second reactor (Figure 1). The yield of butadiene was 18 % (8).

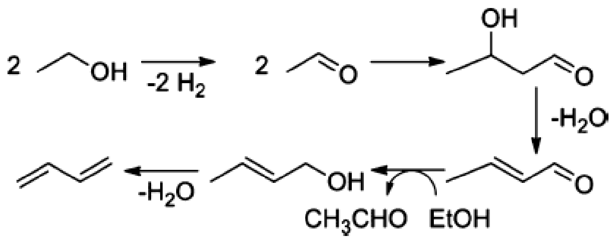

Figure 1. *Overall scheme of butadiene production from ethanol via Ostromislensky conversion (10, 11).*

Lebedev got a 10-13% yield of butadiene using his reaction (7). In 1928-1931, Lebedev proposed the formulation of rubber products from butadiene. In 1929, he received a patent (12) and submitted to the Soviet Ministry of Chemical Industry (Glavkhimprom) a plan of work necessary for the design of an experimental plant. During 1930, an experimental plant was built in Leningrad where in 1931 several hundred kilograms of synthetic rubber was produced (13) and used in the military industry to produce car tires. Later on, the industrial-scale yield of butadiene was improved to 44 % (7, 14).

A variety of metal oxide catalysts, including silica- and alumina-supported single, binary, or ternary metal oxides such as copper and zirconium (15, 16), mixed metal oxide catalysts such as MgO/SiO_2 (9, 17) or ZnO/Al_2O_3 (2) and $Ag/ZrO_2/SiO_2$, Hf–Zn/SiO and ZrBEA zeolite catalysts (16) were investigated.

Based on economic and environment aspects, it has been determined that the Lebedev method holds more potential than the Ostromislensky one (17).

However, it is known that Ipatieff began to study the properties of butadiene much earlier, in 1900-1903. Who was Ipatieff and what did he investigate? What were the reasons that prevented his name from being attached to the reaction?

Low Yield of Butadiene and Search for Catalysts

In 1900-1903, Ipatieff began to study the properties of butadiene, which had been obtained before him only from the pyrolysis of amyl alcohol by Caventou. The only method then reported in the literature was the passage of alcohol vapours through a heated tube (1). While reflecting on the reasons for the small yield of butadiene, Ipatieff experimented with the tube material, the reaction conditions and composition of pyrolysis products. It turned out that amyl alcohol decomposed to form isovaleric aldehyde and hydrogen when an iron tube was used at approximately 600 °C, whereas it went unchanged at the same temperature in glass and porcelain tubes. When the temperature was increased to 700 °C, smaller amounts of aldehyde formed in these tubes with simultaneous formation of significant quantities of carbon monoxide, methane, ethylene, and hydrogen. Ipatieff made parallel experiments with primary, secondary and tertiary alcohols and found out that:

1) All primary alcohols, when passed through an iron tube, form aldehydes and hydrogen.

2) Secondary alcohols decompose into ketones and hydrogen.

3) Tertiary alcohols do not produce any of these products, but decompose into hydrocarbons and water at high temperatures.

In 1901, Ipatieff made a report to the RPhChS on pyrogenetic reactions of organic substances. In this report, for the first time in science Ipatieff pointed out the influence of the material of the vessel walls on the course and products of the reaction (18). This paper was published in a German journal as well (19), as was common practice at the time for Russian chemical researchers.

In this study, catalytic reaction occurred at very high temperature, and that was new since previously it was believed that at temperatures above 500-600 °C no catalytic effect could be expected. In January of 1901 a new catalytic decomposition reaction of alcohols into aldehyde and hydrogen (aldehyde decomposition), which is related to dehydrogenation catalysis, was discovered.

In September of 1901, at the meeting of the RPhChS Ipatieff made a new detailed report on the catalytic decomposition of ethyl alcohol under the influence of various catalysts and presented a hypothesis about the mechanism of the processes taking place. In this report, an important conclusion had been drawn that if the metal causes an aldehyde decomposition, then its oxide should have the same effect (20). Ipatieff confirmed the correctness of this conclusion experimentally on the example of zinc and its oxide.

By continuing the series of experiments on the pyrogenic decomposition of alcohol, Ipatieff discovered that alumina worked as a catalyst for this reaction and introduced it for obtaining olefins from aliphatic alcohol.

At the end of December 1901, the Eleventh Congress of Russian Naturalists and Physicians was held in St. Petersburg. There Ipatieff made a one-hour report, "Further experiments on the decomposition of alcohols under the influence of various contact agents" (21). M. I. Konovalov and I. L. Kondakov noted that the work had practical value. However, they stated that the author of the report did not indicate the dependence of the amount of decomposing isobutyl alcohol on the reaction time. Kondakov also noted that the product obtained from what he expected to be a bromination reaction after decomposition of isobutyl alcohol was apparently butadiene.

In 1903, Ipatieff investigated the mixture of decomposition products of ethanol using aluminum powder (22, 23). In order to separate unsaturated hydrocarbons from a mixture of products (in addition to those mentioned above, CO_2, CO, CH_4 and H_2 were also present), Ipatieff carried out the reaction of unsaturated hydrocarbons with bromine water and obtained a dibromide and a tetrabromide, which had different melting points. Then, the reaction of these bromides with hydrogen bromide in an alcohol solution was conducted in the presence of zinc powder. As a result, an unsaturated monobromide C_4H_7Br discolored bromine water and potassium permanganate solution. The yield of butadiene obtained in Ipatieff's experiments was 1.5-2 %.

During 1904-1907 Ipatieff finally confirmed that at 600 °C in the presence of aluminium powder the pyrolysis of ethyl alcohol yields butadiene in addition to acetaldehyde and ethylene (24-27):

$$CH_3CH_2OH \xrightarrow{\text{Al, p, t}} H_2 + CH_3CHO$$

$$CH_3CH_2OH \xrightarrow{\text{Al, p, t}} H_2O + C_2H_4$$

$$2CH_3\text{–}CH_2OH \xrightarrow{\text{Al, p, t}} H_2 + 2H_2O + CH_2\text{=CH–CH=}CH_2$$

Ipatieff summarized the results of the influence of various catalysts, temperature and pressure on the decomposition of alcohols in his book (28).

Thus, in his studies carried out about 115 years ago, Ipatieff found out the possibility of controlling the selectivity of heterogeneous catalytic reactions. He determined that by changing the catalysts, their composition and temperature, different products could be obtained from the same reagent (ethanol): ethylene, diethyl ether, acetaldehyde, butanol, acetone, butadiene, etc.

Conclusions

The authors of the present paper wanted to help restore recognition to one of the greatest chemists of the 20th century who worked in the field of organic chemistry and who was unfairly forgotten in the course of history.

In organic chemistry, there are a number of reactions bearing the name of the researcher who discovered or investigated the reaction. Often the names of several scientists appear in the name of the reaction: it could be the researchers of the first publication, or researchers of the reaction or scientists who simultaneously published the results of the new reaction. Based on the above material, the authors think that despite low yield of butadiene and not very efficient catalysts it would be quite logical and historically fair to call the reaction of butadiene production from ethanol an Ipatieff-Lebedev reaction, and not just Lebedev reaction. In our opinion, the reason that prevented the use of Ipatieff's name for the reaction was the low yield of butadiene and not very efficient catalysts.

In recent years, Ipatieff's life and research during his time in the United State have been described in more detail. His contribution to the study of terpene transformations (29), of various acid-catalyzed processes that yielded ultra-high-octane fuels used for Air Force planes in World War II (4), and investigations in catalysis including high pressure, dispersion of metals on supports, and the use of promoters (30) have been described.

References and Notes

1. E. Caventou, "Ueber eine mit dem zweifach-gebromten Brombutylen isomere Verbindung und über die bromhaltigen Derivate des Brombutylens," *Ann. Chem.*, **1863,** *127*, 93-97. doi:10.1002/jlac.18631270112.
2. E. V. Makshina, M. Dusselier, W. Janssens, J. Degreve, P. A. Jacobs and B. F. Sels, "Review of old Chemistry and new Catalytic Advances in the on-purpose Synthesis of Butadiene," *Chem. Soc. Rev.*, **2014**, *43*, 7917-7953.

3. J. Grub and E. Löser, "Butadiene," *Ullmann's Encyclopedia of Industrial Chemistry* Wiley-VCH, Weinheim, Germany, 2012. doi:10.1002/14356007.a04_431.pub2
4. M. Jacoby, "Vladimir Ipatieff is the Catalysis Superhero You've never Heard of," *Chem. Eng. News*, **2019**, *97*(*May 11*), 22-24.
5. S. V. Lebedev, "O Poluchenii Divinila Neposredstvenno iz Spirta [On Obtaining Divinyl Directly from Alcohol]," *Zhizn' i Trudy* [*Life and Works*], Leningrad, 1938, pp 491-514.
6. V. F. Tret'yakov, R. M. Talyshinskii, A. M. Ilolov, A. L. Maksimov and S. N. Khadzhiev, "Initiated Conversion of Ethanol to Divinyl by the Lebedev Reaction," *Petroleum Chem.,* **2014**, *54***,** 195-206.
7. V. F. Tret'yakov, A. M. Ilolov, R. M. Talyshinskii, A. M. Gyul'maliev and S. N. Khadzhiev, "Quantum-Chemical and Thermodynamic Analysis of Energy Characteristics of Main Reactions and the Initiator Hydrogen Peroxide in Ethanol to Divinyl Conversion on a ZnO/Al_2O_3 Catalyst" *Petroleum Chem.***, 2017,** *57,* 423-430.
8. I. I. Ostromislensky, "O kondensacii spirtov i aldegidov v prisutstvii vodootscheplaiuschich veschestv i o mechanizme etogo processa," *Zhurn. Rus. fiz.-khim. ob-va,* **1915**, *47*, 1494-1506.
9. G. Pomalaza, M. Capron, V. Ordomsky and F. Dumeignil, "Recent Breakthroughs in the Conversion of Ethanol to Butadiene," *Catalysts,* **2016***, 6*, 203-208.
10. T. De Baerdemaeker, M. Feyen, U. Muller, B. Yilmaz, Feng-Shou Xiao, Weiping Zhang, Toshiyuki Yokoi, Xinhe Bao, H. Gies and D. E. De Vos, "Bimetallic Zn and Hf on Silica Catalysts for the Conversion of Ethanol to 1,3-Butadiene," *ACS Catal.***, 2015,** *5*, 3393- 3397.
11. Q. Zhu, B. Wang and T. Tan, "Conversion of Ethanol and Acetaldehyde to Butadiene over $MgO-SiO_2$ Catalysts: Effect of Reaction Parameters and Interaction between MgO and SiO_2 on Catalytic Performance," *ACS Sustainable Chem. Eng*., **2017**, *5*, 722-773.
12. S. V. Lebedev, "Procédé pour obtenir des dioléfines directement des alcools," French Patent 665,917, issued May 13, 1929.
13. Yu. A. Gorin, *Research of S. V. Lebedev in the Field of Synthesis of Divinyl from Ethyl Alcohol and their Further Development*, Moscow, 1954.
14. A. M. Ilolov, R. M. Talyshinskij and V.F. Tretjakov, "Istoricheskije aspekti odnostasdijijnogo procesa divinila iz etanola," *Istorija nauki i techniki***, 2014,** *4*, 10-14.
15. J. L. Cheong, Y. Shao, S. J. R. Tan, X. Li, Y. Zhang and S. S. Lee, "Highly Active and Selective Zr/MCF Catalyst for Production of 1,3-Butadiene from Ethanol in a Dual Fixed Bed Reactor System," *ACS Sustainable Chem. Eng.*, **2016**, *4*, 4887-4894.
16. S.-H. Chung, C. Angelici, S. O. M. Hinterding, M. Weingarth, M. Baldus, K. Houben, B. M. Weckhuysen, P. C. A. Bruijnincx, "Role of Magnesium Silicates in Wet-Kneaded Silica-Magnesia Catalysts for the Lebedev Ethanol-to-Butadiene Process," *ACS Catal.,* **2016,** *6*, 4034-4045.
17. D. Cespi, F. Passarini, I. Vassura and F. Cavani, "Butadiene from Biomass, a Life Cycle Perspective to Address Sustainability in the Chemical Industry," *Green Chem*., **2016,** *18*, 1625-1638.
18. V. N. Ipatieff, "Pirogeneticheskie kontaktnie reakcii s organicheskimi veschestvami," *Zhurn. Rus. fiz.-khim. ob-va,* **1901**, *33*, 143-149.
19. V. N. Ipatieff, "Ueber pyrogenetische Reactionen organischer Substanzen," *Ber. Dtsch. Chem. Ges.*, **1901**, *34*, 596-599.
20. V. N. Ipatieff, "Pirogeneticheskie kontaktnie reakcii s organicheskimi veschestvami," *Zhurn. Rus. fiz.-khim. ob-va,* **1901**, *33*, 632-643.
21. V. N. Ipatieff, "Dalneichije opiti po razlozeniju spirtov pod vlijanijem razlichnich agentov kontakta," *XI Congress of Russian Naturalists and Physicians,* St. Petersburg, **1902**, 128.
22. V. N. Ipatieff, "Zur Frage über Zersetzung des Äthylalkohols in Gegenwart verschiedener Katalysatoren," *J. Prakt. Chem.*, **1903**, *67*, 420-422.
23. V. N. Ipatieff, "K voprosu o razlozeniji spirta pod vlijanijem razlichnich katalizatorov," *Zhurn. Rus. fiz.-khim.. ob-va*, **1903**, *35*, 449-452.
24. V. N. Ipatieff, "Kataliticeskije reakciji pri visokich temperaturach i davlenijach," *Zhurn. Rus. fiz.-khim. ob-va*, **1904**, *36*, 786-813.
25. V. N. Ipatieff, "Kataliticeskije reakciji pri visokich davlenijach i temperaturach," *Zhurn. Rus. fiz.-khim. ob-va*, **1907**, *39*, 681-692.
26. V. N. Ipatieff, "Kataliticeskije reakciji pri visokich davlenijach i temperaturach," *Zhurn. Rus. fiz.-khim. ob-va*, **1907**, *39*, 693-702.
27. V. N. Ipatieff, V. N. Zdzitoveckij, "Kataliticeskije reakciji pri visokich davlenijach i temperaturach," *Zhurn. Rus. fiz.-khim. ob-va*, **1907**, *39*, 897-901.
28. V. N. Ipatieff, *Kataliticheskie reakcii pri visokich temperaturach i davlenijach. 1901-1907*, M. P. Frolova, St. Petersburg, 1907, p 170.
29. C. P. Nicholas, **"**Terpene Transformations and Family Relations: Vladimir Ipatieff," *Bull. Hist. Chem.*, **2019**, *44***(**2), 116-122.
30. C. P. Nicholas, "Dehydration, Dienes, High Octane, and High Pressures: Contributions from Vladimir Nikolaevich Ipatieff, a Father of Catalysis," *ACS Catal.*, **2018**, *8*, 8531-8539.

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2020 Conferences in History and Philosophy of Chemistry: Update

• International Committee for the History of Technology (ICOHTEC): 47th annual meeting scheduled for Eindhoven, the Netherlands ~~July 13-19~~
https://icohtec2020eindhoven.org
The conference will be an abbreviated online event, July 15-17

• International Society for the Philosophy of Chemistry: 24th annual meeting scheduled for Buenos Aires, Argentina ~~July 21-23~~
http://www.filoexactas.exactas.uba.ar/ispc2020/
Postponed to 2021, date not yet selected as of late May 2020

• European Society for the History of Science (ESHS): 9th International Conference, hosted by the Centre for the History of Universities and Science at the University of Bologna (CIS) and by the Italian Society for the History of Science (SISS), scheduled for Bologna, Italy, August 31-September 3
https://sites.google.com/view/eshsbologna2020
This conference will be held online

• ACS Division of the History of Chemistry at the Fall 2020 National Meeting of ACS, San Francisco, California, August 16-20
www.acs.org/content/acs/en/meetings/national-meeting.html
HIST has cancelled its program and will reschedule symposia at future conferences. As for the larger conference, ACS states (as of late May):
What we can assure you is that the ACS Fall 2020 National Meeting & Expo will take place in one form or another. We are exploring various scenarios to allow for a safe and meaningful exchange of scientific research and information, as well as networking; all things normally associated with an ACS national meeting. Those scenarios range from an in-person event to a mix of in-person and virtual activities to an all virtual event.

• History of Science Society jointly with the Society for the History of Technology (SHOT), October 7-11 in New Orleans, Louisiana, USA
https://hssmeeting.org
As of late May 2020, this event appears to be on schedule to proceed.

• Pacifichem 2020: The International Chemical Congress of Pacific Basin Societies, December 15-20 in Honolulu, Hawaii, USA
https://pacifichem.org
This conference is scheduled to have a historical symposium, and as of late May 2020 it appears to be on schedule to proceed.