TERPENE TRANSFORMATIONS AND FAMILY RELATIONS: VLADIMIR IPATIEFF (1)

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Introduction

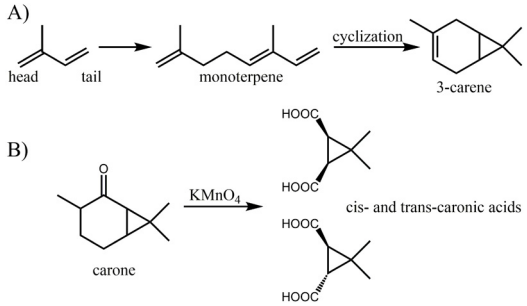
At the Fall 2018 American Chemical Society (ACS) Meeting in Boston in the Symposium in honor of David Lewis, I presented on the Russian chemist Vladimir Nikolaevich Ipatieff's contributions to the development of catalytic chemistry both before and after emigrating to the United States. From some of that work, a basic biographic sketch and an account of Ipatieff's most important catalytic discoveries was recently published in *ACS Catalysis* (2) and highlighted in *Chemical & Engineering News* (3). Ipatieff is a major figure in the Russian chemical diaspora and much has been previously written about him (4, 5, 6). Here, I expand on Ipatieff's work at Northwestern University, particularly in the field of terpene chemistry, and his relationship with family members, including his wife Barbara and half-brother Lev Chugaev.

Russian Life and Early Terpene Experiences

Born in Moscow November 21, 1867, the son of the architect Nikolai Alekseevich Ipatieff, and schooled at the Mikhail Artillery Academy in St. Petersburg, Vladimir Ipatieff graduated in 1892 before returning to Moscow to marry Barbara Dmitrievna Ermakova, who would be partnered with him until their deaths in late 1952 (4).

After teaching near Moscow for a year, Ipatieff returned to St. Petersburg to research with A. E. Favorsky at the University of St. Petersburg before receiving a scholarship from the Russian government to study abroad in Germany with the group of Adolph von Baeyer. This experience set the tone for much of Ipatieff's future work due to the people he became acquainted with and the science pursued.

The project assigned in Munich was to determine the structure of carone, a monoterpene ketone derivative. Monoterpenes have the formula $C_{10}H_{16}$ and are biosynthetically prepared via head to tail polymerization of isoprene (Scheme 1) (7). Significant questions for investigation often involved structure, reactivity, and location of oxygenate functional groups and were of interest to investigate transformations of organic molecules throughout the length of Ipatieff's career.

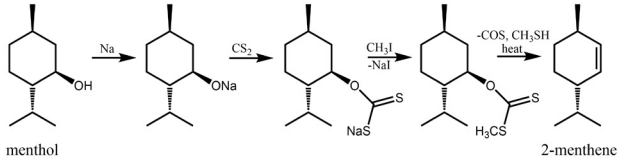


Scheme 1*. Terpene biosynthesis is shown in part A and the oxidation of carone to caronic acids in part B.*

While von Baeyer had been working with carone (8), and Wagner had previously suggested a structure (9), it was Ipatieff's work utilizing oxidation to caronic acids

with $KMnO_4$ that proved the structure (10). The *cis*- and *trans*-caronic acids could be separated, with the ratio of *cis*- to *trans*- corresponding to the stereochemistry of the original carone, while also allowing confirmation of the presence of a cyclopropane ring in carone. Following the conclusion of his fellowship with von Baeyer in late 1896, Ipatieff returned to Russia to begin a very successful career researching in St. Petersburg.

One of Ipatieff's acquaintances from Moscow was Lev Chugaev, also a chemist (11). While Chugaev is best known as an originator of coordination chemistry for his work on platinum complexes, he worked in many fields (12, 13). Just prior to 1900, Chugaev worked on reacting deprotonated terpene alcohols with CS_2 to form xanthogens which could be distilled to form a single hydrocarbon compound, (Scheme 2) thereby greatly enhancing terpene structural understanding.



Scheme 2. *Conversion of menthol to 2-menthene via the xanthenogen route pioneered by Chugaev.*

As the two famous chemists talked during Chugaev's move from Moscow to St. Petersburg University in 1908, he and Ipatieff discovered they were half-brothers, children of Anna Aleksandrovna Gliki six years apart (14). Anna had fallen for the science teacher Aleksandr Fomich Chugaev at the girls school she attended, but was not allowed to marry him for economic reasons. Instead, she married Nikolai Ipatieff. About 5 years after Vladimir's birth, Anna left the family to join A. F. Chugaev with whom she had Lev Chugaev. Shortly thereafter, she returned to live with the Ipatieffs before dying of tuberculosis in 1880, just before Vladimir turned 13. Both Chugaev and Ipatieff wrote warmly of their mother and it is amazing she is the parent of two well-regarded chemists (15).

Like many Russians of the time, Ipatieff had a beard throughout his life in Russia, usually of quite impressive character. Early in his career, Ipatieff spilled a few drops of isobutyric acid into his beard, an event which kept Barbara at a distance for days (16a). Perhaps due to this, the beard shortened over the years, and upon leaving Russia permanently, Ipatieff shaved his beard as a new start to life, and was clean-shaven thereafter (17, 18a).

Figure 1. *Photographs of Vladimir Ipatieff over the course of his career. A) 1897 during his stint with von Baeyer. B) as General Lieutenant in 1914. C) Pre-1917, but likely 1916 upon election as an ordinary academician. D) Early 1930s while at UOP. E) in 1942, shown with his wife Barbara. Photos D and E are reproduced with permission from the ACS from references 2 and 19, respectively.*

Travel to USA and Work with UOP

At the 1930 World Power Congress in Berlin, Ipatieff was introduced to the head of Universal Oil Products (UOP) research, Gustav "Gasoline Gus" Egloff by Hans Tropsch. Egloff was seeking to start a catalytic research program at UOP and Ipatieff agreed to visit. At the age of 63, Ipatieff left Barbara in Berlin for the summer and traveled by ship from Cherbourg, France, to New York City in the last second-class berth available on the Bremen IV (18b).

After meeting with Hiram Halle, the President of UOP, in New York, Ipatieff came to Chicago to see the operation. Chicago was, in 1930, a booming place: the second largest city in the United States and the 6th largest in the world with a population of 3,376,438 at the census time (20). The UOP Chicago office was then located in the middle of it all on the 21st floor of the Straus Building, a Graham, Anderson, Probst & White designed structure that was one of the first two Chicago buildings over 260 ft in height (Figure 2).

Figure 2*. The Straus Building, located at 310 S. Michigan Avenue, Chicago, IL (corner of Jackson and Michigan). Photograph from the Art Institute of Chicago's Ryerson & Burnham Historical Archival Image Collection.*

While the drafting, sales and CEO offices were in downtown Chicago (the CEO's office was in the northeast corner looking out onto Grant Park and Lake Michigan), the newly constructed $500,000 research facility (21) was located southwest of Chicago in the suburb of Riverside on what at that time was Route 66. It had three buildings on the corner of the lot with trees to approximate a quiet college campus and was co-located with a small independent oil refinery to serve as the demonstration location for newly developed technology. Ipatieff was driven out to Riverside for discussions about leading research at UOP, reporting in his memoir (18c):

> I saw at once that no real scientific work was being done here and that before us was a virgin laboratory, unfertilized by chemical thought and unadapted to work on catalysis and high pressures.

At an age when most would have considered retirement, lacking knowledge of English, and given these comments, Ipatieff surprisingly agreed to return the next summer to lead research programs at UOP. Between the difficulty of acquiring a US visa for a Russian in the period between the two World Wars, tension in Germany, and the significant compensation offered (22), the prospect of building catalysis at UOP while lecturing part-time at Northwestern was a good offer.

Returning to Europe in the fall of 1930, Ipatieff continued previously contracted work for Bayerische Stickstoff Werke. With the help of Ward Evans, Chair of Chemistry at Northwestern University, Ipatieff was afforded a work visa in exchange for delivering a lec-

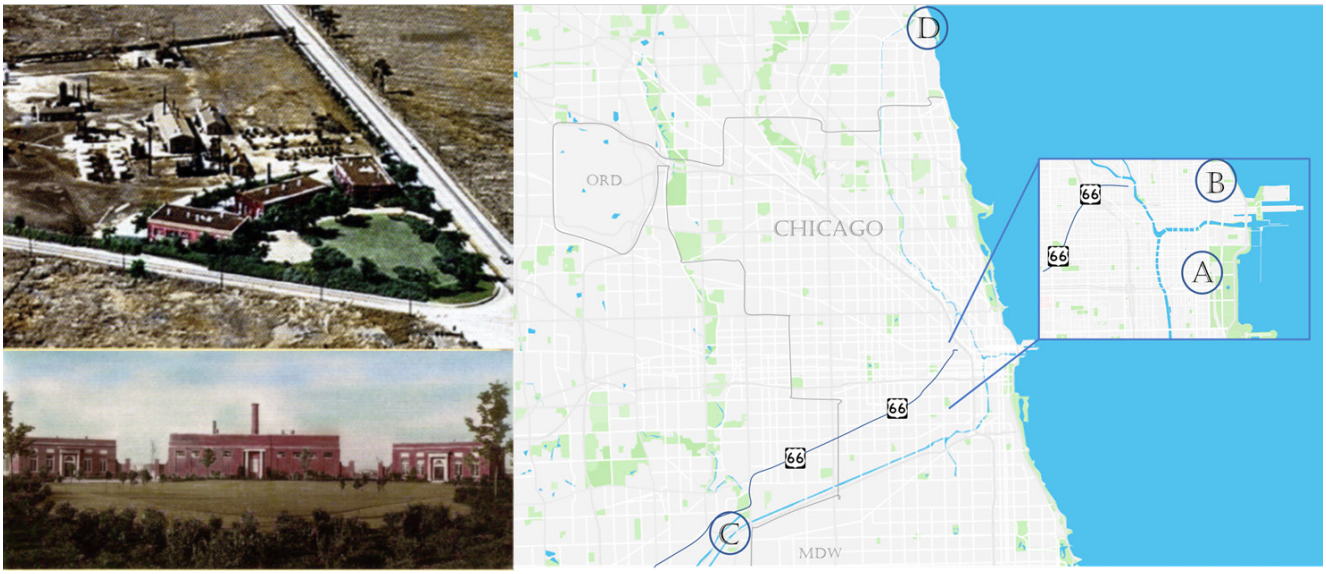


Figure 3*. The upper left shows an aerial view of the Riverside facility showing the "university campus" in the foreground and the refining development area behind. The bottom left shows the "three imposing buildings" comprising the research facility. The right side shows a map of Chicagoland and an inset of downtown marked with the locations of A) the UOP Chicago office, B) the Pearson Hotel, where the Ipatieffs lived, C) the UOP Riverside facility, and D) Northwestern University (25). Left images courtesy of UOP and the Chicago Aerial Survey.*

ture series at Northwestern in 1931-32. In the spring of 1931, he, Barbara, and another woman, Alexandra "Shura" Seldowitsch sailed from Berlin to New York City in a first-class cabin on the S. S. Columbus (18d, 23).

After arriving in Chicago, the three took a two-bedroom suite in the Pearson Hotel, the women in one bedroom and Ipatieff in the other (24). The Pearson was located on the north side of downtown at Chicago and Michigan Avenues, now the site of Water Tower Place. From the Pearson Hotel, Ipatieff had easy access to Route 66 via Chicago Avenue and was driven out to Riverside daily until named Research Professor at Northwestern University in 1937, when he split time by commuting 2-3 times a week north to the Evanston campus to teach and research there. (Figure 3).

While the true nature of the relationship between the Ipatieffs and Seldowitsch will never be known, this did not stop the Hearst papers from putting out headlines in November of 1932 entitled "Northwestern Professor in Love Tangle" after Ipatieff was sued in US court by Gregory Seldowitsch for "loss of affection" (26).

The legal dispute was quickly thrown out and appears not have hindered the scientific output of Ipatieff or significantly shaken his relationship with Barbara. The discoveries that he, Herman Pines, and Vladimir Haensel made were of importance to UOP and to the USA, generating 8,790 US and foreign patents from 1921-1955. For this productivity, the Riverside facility (Figure 2) was named a National Historical Chemical Landmark in 1995 (21).

Among the discoveries Ipatieff participated in were three previously highlighted acid-catalyzed reactions: oligomerization, aromatic alkylation, and paraffin alkylation, all three of which were used to make 100 octane fuel during World War II (2, 6).

Meanwhile, Ipatieff researched and taught at Northwestern from 1937, the same year he and Barbara became US citizens, shortly after having their Soviet citizenship revoked (4). To start the Northwestern lab, Ipatieff personally funded much of the laboratory equipment while UOP paid salaries. The early years were fraught with every manner of dispute between university and corporation (16b), but were solved in 1942 when the laboratory moved from University Hall to the newly built Technological Institute (Figure 4) and was inaugurated as the Ipatieff Teaching Laboratory. To distinguish work carried out at Northwestern from that at UOP, Ipatieff often worked with molecules not present in crude oil fractions. Significant among these were the terpenes Ipatieff first encountered in Germany.

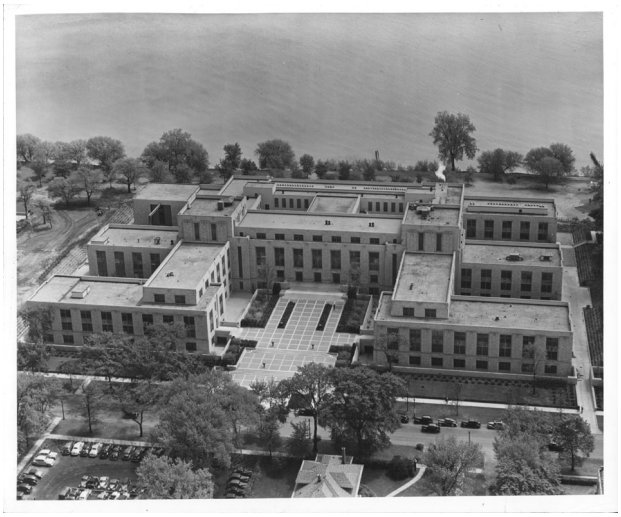


Figure 4*. Exterior aerial view of Northwestern Technological Institute in 1942. Photo courtesy of the Northwestern University Archives.*

He and Herman Pines started their terpene work by studying the dehydration of alcohols to alkenes (27). From this initial 1944 publication until Ipatieff's death in 1952, the pair collaborated on twenty papers covering reactivity patterns of the terpenes, with Pines extending the series until 1959. While Ipatieff's initial work in terpenes was largely structural in character, he now focused primarily on reactivity patterns.

The dehydration work was designed to probe C–H reactivity by understanding the location of double bonds formed, though this led to a study of carbocation stability once Ipatieff and Pines determined that alkyl shifts also occurred during catalysis (28, 29).

Among other interesting discoveries were a method for determining ring structure and size for an unknown terpene. Ipatieff and Pines heated terpenes including cyclofenchene, isocamphane, and isobornylane in the presence of 1-2% aqueous $MgCl_2$ to learn which size rings were most susceptible to cleavage.

From this work, they concluded that cyclopropanes such as that found in the carene or cyclofenchene structures ring-opened most readily, and that six-membered rings were most stable. Other size rings opened at intermediate temperatures. This knowledge was used to predict, and helped confirm, the structure of 2,6-dimethylbicyclo[3.2.1]-2-octene, a new terpene that Ipatieff had observed during solid phosphoric acid (SPA) catalyzed isomerization of limonene (30, 31). SPA was invented

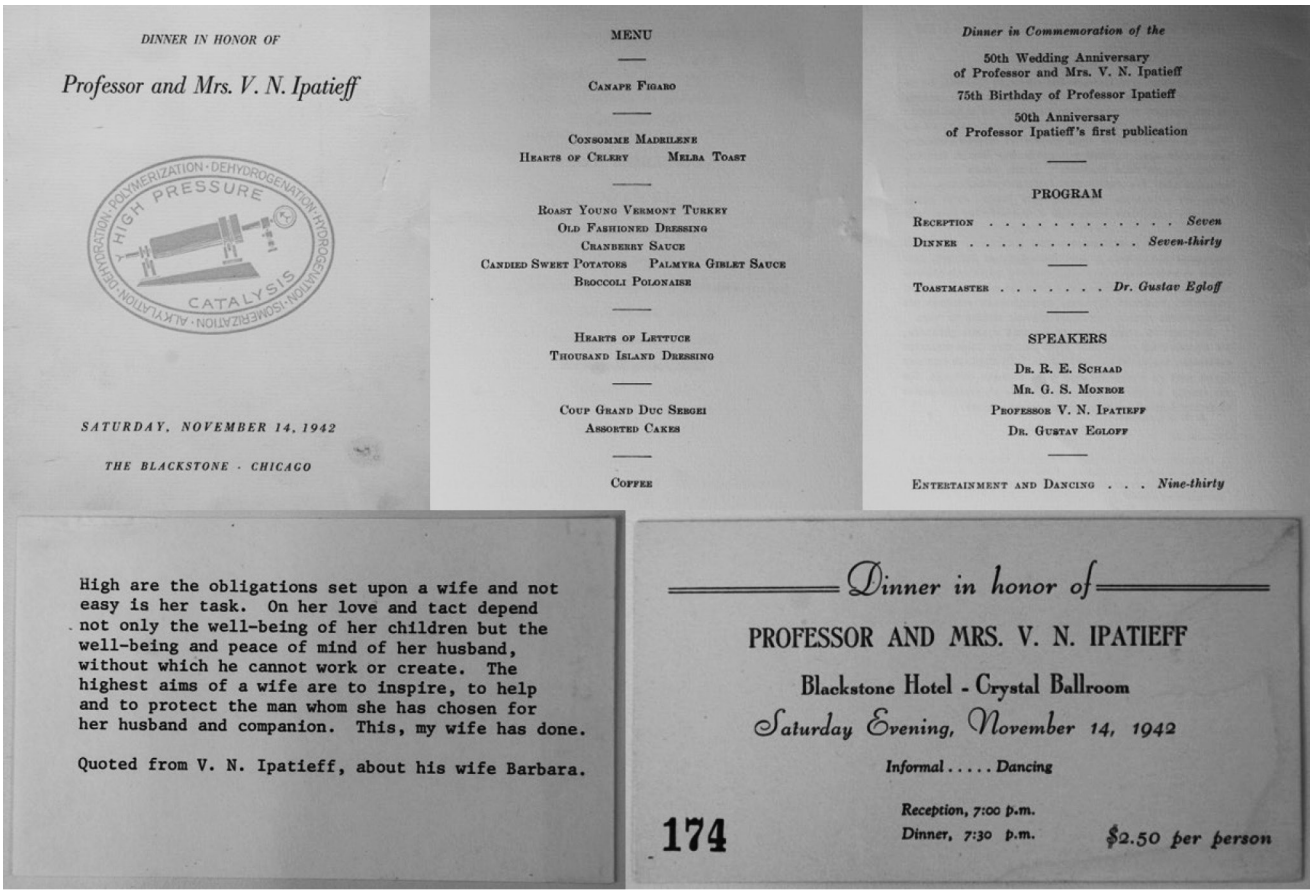


Figure 5*. The invitation, menu, and program from the November 14th, 1942, dinner in honor of Professor and Mrs. Barbara Ipatieff. At the bottom of the composite are two inserts into the invitation: a quote from Ipatieff about his wife Barbara and the invitation card (35).*

by Ipatieff by combining a silica source with H_3PO_4 and extruding the mixture and is still produced commercially today for acid catalyzed reactions (32). He was even able to propose a mechanism for the formation of the new terpene which depended on the concentration of limonene in the reaction.

Hydrogenation was also frequently studied using the high-pressure autoclaves that Ipatieff had previously developed (33). He utilized particular steels to fabricate autoclaves where thin Cu metal seals were held between knife edges on the top and bottom of the autoclave. These autoclaves were the first apparatus to allow reactions at pressures up to 1300 atm to be investigated.

With discoveries of historic importance, patents, and papers from this US work adding up, in addition to accomplishments in Russia, accolades arrived, including election to the National Academy of Sciences in 1939 (4). One such accolade for Ipatieff was a dinner (Figure 5) in late 1942 hosted by UOP to commemorate the 50th wedding anniversary of him and Barbara, his 75th birthday, and the 50th anniversary of his first paper (34).

Interestingly, a card was inserted into the menu / program describing the respect Ipatieff had for Barbara and her ability to ensure life was taken care of so that he could continue discovering new science. Ipatieff appears to have consistently consulted Barbara about life decisions. As they left Russia in 1930, he reports a conversation wherein they discuss returning to Russia, but both suspect it may not be their fate to return (18e).

Later, on Christmas Eve 1936, the Ipatieffs received a cable from their two children remaining in Russia noting that the Ipatieffs must return to Russia immediately, or the children would not be responsible for the consequences. Ipatieff gave Barbara the ultimate decision in whether they would return. They chose not to, with Barbara reasoning that to do so would mean a death sentence for Ipatieff and that the children would

be worse off, likely sent to a distant place (18f). As Paul Haensel wrote (5):

> For him and his wife, in their private life, emigration was a cruel experience, however. The Soviet government resented Ipatieff's "flight" and proclaimed him a traitor of his country. His own son, Vladimir, a gifted chemist and professor in Leningrad, had to renounce his father. His only daughter has no possibility to see her aged parents, nor have the grandchildren. The Ipatieffs lost a son, a brilliant young biologist, during the World War in action. Another son perished during a research study fighting malaria in the Belgian Congo.

Through it all, Ipatieff kept developing notable new chemistries regardless of the cruelties of life. For the Ipatieffs, having to continue working toward the end of their lives in conditions they would never have tolerated previously seems to sum up the inequities life threw at them (18g).

Vladimir and Barbara died 10 days apart, on November 29th and December 9th 1952. They were married for 60 years, and had known each other for 70 of his 85 years after having met at a summer resort in Russia as pre-teens (6).

References and Notes

1. Presented at the 256th National Meeting of the American Chemical Society, Boston, MA, Aug. 21, 2018, HIST 23.
2. C. P. Nicholas, "Dehydration, Dienes, High Octane, and High Pressures: Contributions from Vladimir Nikolaevich Ipatieff, a Father of Catalysis," *ACS Catalysis*, **2018**, *8*, 8531-8539. https://pubs.acs.org/doi/10.1021/acscatal.8b02310
3. M. Jacoby, "Vladimir Ipatieff is the Catalysis Superhero You've Never Heard of," *Chem. Eng. News*, **2019**, *97(May 11)*, 22-24.
4. L. Schmerling, "Vladimir Nikolaevich Ipatieff, 1867-1952," *Biogr. Mem. Natl. Acad. Sci. U.S.A.*, **1975**, *47*, 83-142.
5. P. Haensel, "V. N. Ipatieff in Russia," *Chem. Bull.*, **1940**, *27(4)*, 109-113. Published by the Chicago Section of the ACS, digitized by Northwestern University.
6. P. Hampson, "The Road to Success: A Sketch of Vladimir Ipatieff, Famed Oil Scientist," *Chicago Tribune*, Sept. 27, 1952, p 35.
7. J. L. Simonsen and D. H. R. Barton, *The Terpenes: the Sesquiterpenes, Diterpenes, and Their Derivatives*, Cambridge University Press, 2nd ed., Cambridge, UK, reprinted 1952.
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12. G. B. Kauffman, "Terpenes to Platinum: The Chemical Career of Lev Aleksandrovich Chugaev," *J. Chem. Educ.*, **1963**, *40*, 656-665.
13. D. E. Lewis, *Early Russian Chemists and Their Legacy*, Springer, Heidelberg, Germany, 2012, "Into a New Century: Chemists Advancing the Legacies of Kazan, St. Petersburg, and Moscow," Ch. 5, section 5.3.2.1.
14. V. N. Ipatieff, *The Life of a Chemist: Memoirs of V. N. Ipatieff*, Stanford University Press, Stanford, CA, 1946. The book was translated by V. Haensel and R. Lusher, and edited by X. J. Eudin, H. D. Fisher and H. H. Fisher, from his memoirs written in Russian.
15. In Ipatieff's memoir of his time in Russia (Ref. 14) not a single reference to his father his made, but many times he writes of his mother and qualities she taught him.
16. H. Pines, *Genesis and Evolution of the Ipatieff Catalytic Laboratory at Northwestern University 1930-1970*, Department of Chemistry, Northwestern University, Evanston, IL, 1992. a) p 109. b) Ch. 1.
17. See the transformation in Figure 1 from images A-C to D & E. Also in Ref. 2 from Figure 2B and 2D to the well-known picture of Ipatieff as Lieutenant General to Figures 4, 5, 8, and 10, all of which are after Ipatieff's arrival in the US.
18. V. N. Ipatieff, *My Life in the United States: The Memoirs of a Chemist*, Northwestern University Press, Evanston, IL, 1959. Translated and edited from his memoirs largely written in Russian, but from a mixture of languages. a) p 111. b) p 9. c) p 16. d) p 29. e) p 6. f) p 106. g) p 82.
19. *Chem. Eng. News*, **1947**, *25(12)*, 829. https://pubs.acs.org/doi/10.1021/cen-v025n012.p829.
20. *Growth of the World's Urban and Rural Population, 1920-2000*. Department of Economic and Social Affairs, United Nations, New York, 1969.

    From Annex V: New York, London, Paris, Tokyo, Berlin, Chicago, Ruhrgebeit polycentric urban area, Buenos Aires, Philadelphia, Osaka were the top 10.
21. The campus and the three neoclassical buildings designated as a National Historical Chemical Landmark were

designed by Holabird and Root. https://www.acs.org/content/acs/en/education/whatischemistry/landmarks/uoplaboratory.html (accessed Nov. 1, 2019).

22. Ipatieff was the 3rd highest paid ($21,500) employee at UOP in 1931-1935 with only Joseph G. Alther (CEO) and Egloff (CTO) paid more. This situation likely continued throughout Ipatieff's tenure with UOP, but I have not viewed payroll records post-'35.
23. Ipatieff neglects to mention Shura in his memoir, but shipping manifest and newspaper photos confirm this. Given Ipatieff's propensity for philanthropy, Shura could have simply been escaping a bad marriage.
24. C. Remsberg and H. Higdon, *Ideas for Rent: The UOP Story*, UOP, Des Plaines, 1994.
25. The Chicago border shown in gray is today's approximate border; the only substantive change to the border from 1930 when Ipatieff arrived in Chicago is the annexation of the land for O'Hare airport (ORD).
26. The *Chicago Examiner* published this title on Nov. 13, 1932. Similar stories were published in Lee Syndicate Papers from the AP wire. *Wisconsin State Journal*, Sunday, Nov. 13, 1932, pp 1 and 4 is one example. They used a headline of "Professor's Wife Aided Mate's Love Theft, Claim." Newspapers transliterated foreign names into English, so both the first and last names of the Seldowitsches have multiple spellings depending on source. Mrs. Ipatieff's name is usually spelled Barbara, but is other times spelled as Varvara.
27. V. N. Ipatieff and H. Pines, "Studies in the Terpene Series. I. Dehydration of Alcohols in the Terpene Series Under Pressure and in the Presence of Dilute Aqueous Salt Solutions," *J. Am. Chem. Soc.*, **1944**, *66*, 1120-1122.
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29. V. N. Ipatieff, G. J. Czajkowski and H. Pines, "Studies in the Terpene Series. XV. Cycloisomerization of α- and β-pinene, α-terpineol, and 1,8-terpin Hydrate," *J. Org. Chem*., **1952**, *17*, 1431-1436.
30. V. N. Ipatieff, H. Pines, V. Dvorkovitz, R. C. Oldberg and M. Savoy, "Studies in the Terpene Series. VI. Cyclic Isomerization of Limonene," *J. Org. Chem.*, **1947**, *12*, 34-42.
31. V. N. Ipatieff, J. E. Germain, W. W. Thompson and H. Pines, "Studies in the Terpene Series. XII. Cyclic Isomerization of Limonene. Proof of the Structure of a New Bicycloterpene," *J. Org. Chem.*, **1951**, *16*, 272-285.
32. C. P. Nicholas, "Applications of Light Olefin Oligomerization to the Production of Fuels and Chemicals" *Appl. Catal. A* **2017**, *543*, 82-97.
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34. V. N. Ipatyev, "Opyt Khimicheskogo Issledovaniia Struktury Stali," *Artilleriiskii zhurnal*, *1892*, No. part I, 937−954.
35. Original invitation held in the UOP Historical Archive. Another copy of the dinner program is part of the holdings at Northwestern University.

About the Author

Chris earned a B.A. at Kalamazoo College (Kalamazoo, MI) before coming to the Chicago area. He has a long history with Ipatieff, having earned his Ph.D. at Northwestern while studying with the 4th Ipatieff professor, Tobin Marks. Wolfgang Sachtler, the 3rd Ipatieff professor, was also part of his committee. In 2006, Chris joined the industrial portion of Ipatieff's US legacy, what is now Honeywell UOP. Chris has worked throughout the Research departments at UOP, primarily focused on inventing and catalytically testing new materials and processes. Particular foci have included heterogeneous catalytic processes, synthesis of inorganic materials, process engineering, molecular adsorption, and olefin metathesis. Chris is an inventor or co-inventor on more than 75 US and foreign patents and coauthor of 25+ peer-reviewed journal articles and a book chapter. A favorite project at UOP has been attempting to replace solid phosphoric acid, a material Ipatieff invented and which is still sold commercially, as the catalyst for olefin oligomerization.