
Another Early Root of Physical Organic Chemistry

Pierre Laszlo*

This paper deals with building an identity for the new sub-discipline of physical organic chemistry. It addresses its historiography: a consequence of Whig history, as pervasive as it is implicit, is the standard account of the rise of a field. It is ascribed in this case to Hughes and Ingold in the 1930s and to Louis P. Hammett's *Physical Organic Chemistry* (1940). The standard account often masks or omits earlier and nevertheless seminal publications. To turn to the historical long haul—the *longue durée* dear to Fernand Braudel—offers a better perspective. I have drawn attention already to Sidgwick's contribution at the very beginning of the twentieth century with *Organic Chemistry of Nitrogen*.

Here, I turn up an even earlier milestone. Linear free energy relationships come close to a defining feature of physical organic chemistry, ever since Hammett's monograph. But when did they originate? Indeed the historical long haul provides the answer.

To evaluate the relative strengths of organic acids was a priority during the second half of the nineteenth century, even before the contributions by Arrhenius and Sørensen. A key episode was Wilhelm Ostwald's 1884 paper, introducing a novel measurement of acidity. It did so by first mining the history of chemistry and rediscovering Wilhelmy's work from 1850. It gave Ostwald the clue he needed to devise a measurement of the strength of acids, from their ability at catalyzing sucrose inversion. Thus, he correlated thermodynamics (acid strength) with kinetics (reaction rates). Hence the importance of this breakthrough as an antecedent, *avant la lettre*, to physical organic chemistry.

Introduction

Fragmentation of the scientific enterprise into sub-disciplines is also a structuring process. It involves defining a more or less virgin field of study, an innovative set of methodologies for studying that field. Most important, the new subdisci-

* Ecole polytechnique, Palaiseau and University of Liège; Emeritus: «Cloud's Rest,» Prades, F-12320 Sénègues, France. pierre@pierrelaszlo.net

pline gives itself both principles and aporias, that is to say, its blind spots: assumptions which, as a rule, are manifestly untrue but turn out to be necessary simplifications.

In retracing the origins of a subdiscipline, some of the main relevant questions concern the pioneers, their social and disciplinary context, and of the time of occurrence of the key or supposedly key events. Other important and related questions are those of possible influences from nearby disciplines, such as for chemistry, physics or biology; the relevant forces, whether individuals were involved or whether it was collective activity, the result of some dominant intellectual configuration or fashion; quantitative evidence, such as crystallization of a number of subdisciplines when a discipline becomes heavily populated; the attendant question of clans with their respective leaders, who may introduce differing and sometimes conflicting research styles.

The subdiscipline focussed upon here is physical organic chemistry. The standard account of its coming into existence stresses Hughes and Ingold's work in England during the 1930s;^{1,2} publication by the American Louis P. Hammett of a book entitled precisely *Physical Organic Chemistry* in 1940; and frequent statements about work by lone pioneers, especially Arthur Lapworth and Arthur Michael at the end of the nineteenth-beginning of the twentieth century.

For full disclosure, I should make it clear that I was a physical organic chemist for the whole duration of my career as an active scientist, from 1960 until 1999. Moreover, I have already published a companion paper on another early root of physical organic chemistry, dealing with publication in 1910 of Sidgwick's book, *Organic Chemistry of Nitrogen*.³

The approach chosen

Linear free energy relationships will serve as our guides. They were a standard and a most important tool in physical organic chemistry.^{4,5,6,7} They embody a correlation between thermodynamics and kinetics. Those are not necessary correlations, logically speaking. They are empirical, part and parcel of an aporia which indeed is one of the foundations of physical organic chemistry. Such correlations were rooted in a study by Wilhelm Ostwald, who himself founded physical chemistry, the predecessor to physical organic chemistry: that is the point I wish to bring up and to stress.

The paper involved⁸ was published when Ostwald was 30 years old. He had been appointed a professor at the Riga Polytechnic three years earlier. At that time,

Ostwald was very much outside the mainstream of organic chemistry. He was an outsider geographically, he had studied at the University of Dorpat, under Russian rule, at a big distance from the great German centers of chemistry. Dorpat is a city to the northeast of Riga. Both towns were already part of the same Livonian Confederation from the Late Middle Ages.

Moreover, whereas his contemporaries concerned themselves with novel substances and reactions, Ostwald's concerns were more fundamental. He strove to understand the forces at work in holding molecules and in determining reactivity.

The French physicist Biot, the inventor of polarimetry, had discovered sucrose inversion, *i.e.*, the hydrolysis into glucose plus fructose. He also found that the transformation is catalysed by acids.⁹ Several decades later, Berthelot would report that the same process is also catalyzed by enzymes, such as invertase, as he termed it because of its action.^{10,11} The 1870s and 1880s were a period when organic chemists were striving to find an objective means for measuring the relative strength of acids. Ostwald's idea was to exploit the hydrolysis of sucrose, to measure its rates under catalysis by various acids and thus to gauge their strengths.

His was a meticulous study, indeed one finds abundant reference in the subsequent literature to the data he gathered. Ostwald studied the catalytic activity of no fewer than 32 different acids, of various structural types.

He used polarimetry for this purpose. Ostwald chose this technique simply because this was how Biot had discovered sucrose inversion. The technique is well-suited for monitoring the phenomenon. The reaction is slow enough, at room temperature, that it can be followed for several hours. Moreover, the observation technique not only is non-destructive, it does not interfere in any way with the progress of the reaction.¹² In addition, the intervening decades, since the first polarimeters were built in Paris by Soleil and his son-in-law Duboscq, had seen major improvements in design.¹³ The instrumentation available to Ostwald was easy to use, quite accurate and furthermore recourse to the sodium D line made it monochromatic.¹⁴ Ostwald used a Laurent-type polarimeter,¹⁵ built in Berlin by Franz Schmidt and Herrmann Haensch, who had set-up their instrument-making company in 1864.

Ostwald's historical erudition

Let me call attention to a most interesting feature of Ostwald's personality. He was acutely interested in the history of the discipline. He knew its bibliography

inside out. Thus, there were at least two antecedents to his work which he was well aware of, and which he refers to explicitly in his paper. Let us now consider them. His paper starts with a quotation from Biot's paper, which Ostwald reproduces in the original French.

The text of the Biot quote reads: "*Des observations comparatives, faites ainsi sur divers acides employés à des doses connues, liées à leurs poids atomiques, présenteraient vraisemblablement des résultats très dignes d'intérêt; mais je n'avais ni les moyens ni les connaissances nécessaires pour les suivre fructueusement sous ce rapport.*" Ostwald chose to read these lines from the French physicist in a prescriptive and programmatic sense: his own work will fulfill the void, glimpsed by Biot and which he had been unable to fill.

The second paper that Ostwald quotes had another physicist for its author. Ludwig Wilhelmy was working in Berlin. This young scientist was independently wealthy, which enabled him to purchase one of the early research polarimeters.¹⁶ He applied it to the phenomenon of sucrose inversion.¹⁷ In so doing, Wilhelmy discovered mass action law. However, his groundbreaking study fell into oblivion, he was not a chemist and in the 1850s and 1860s chemical science had other, major interests, at a distance from kinetics. This was the period for the blossoming of structural theory. Mass action law was rediscovered by Guldberg and Waage in 1864 which further pushed Wilhelmy's contribution into oblivion.¹⁸ When van't Hoff was about to publish in 1884, unbeknownst to him, a near duplicate of Wilhelmy's paper, Ostwald, who knew his chemical history, had to warn him off.

The aftermath

The contemporary context was ionic dissociation theory: after Arrhenius wrote his doctoral thesis on the conductivity of electrolytes. The significance of van't Hoff's *i*-factor, the multiplier necessary to make the gas law extendable to solutions, was pointed out by Arrhenius, but Ostwald made it much clearer than Arrhenius had been able to do.

Ostwald contributed significantly to ionic dissociation theory. He would point out in 1887 that osmotic pressure is proportional to the number of the dissolved particles, and he would formulate the same year 1887 the dilution law, which he showed to be applicable to several hundreds water-soluble acids and bases. In so doing, Ostwald again helped to clarify and extend the concepts of both Arrhenius and van't Hoff.

When Ostwald launched the discipline of physical chemistry and the attendant journal, *Zeitschrift für Physikalische Chemie* the same epochal year 1887,¹⁹ there

was no move of his to set-up a sister or a daughter sub-discipline of physical organic chemistry.

When he turned to kinetic data for measuring the relative strengths of organic acids, this was an astute means for answering a then burning question. In so doing, Ostwald was bridging thermodynamics and kinetics in a way which was rediscovered only half-a-century later, with the first instalments of formal physical organic chemistry. Linear free energy relationships tap into the same vein that Ostwald had pioneered.

Why then has Ostwald's role as an effective founder of physical organic chemistry not been properly recognized? There are two answers to this question. The first, already alluded to, is that his founding physical chemistry just a few years later has totally eclipsed his 1884 contribution linking thermodynamics and kinetics. The second is the embedding in textbooks of Ostwald's study of sucrose inversion as catalyzed by acids: as a classic of chemical kinetics already in the years to follow.^{20,21,22,23,24,25} Moreover, it entered the teaching laboratory as an experiment which most students of organic and / or physical chemistry –the latter especially, for a reason too obvious to be commented upon– repeated for many generations. It was inexpensive in materials. It served as an initiation into a powerful physical method, polarimetry, and it taught students how to use a polarimeter. Sucrose inversion was slow enough that the transformation could be monitored over several hours. Last but not least, it served implicitly as a celebration of one of the giants of chemical science. As a selection of just a sampling of textbooks and of articles in chemical education shows, Ostwald's study of sucrose inversion became statufied as a landmark in the training ritual for students of chemistry.^{26,27,28,29,30,31,32,33,34,35,36,37,38,39,40,41} Its very enshrining as a milestone of chemical kinetics shrouded it; it was not viewed (as it might have) as bridging thermodynamics and kinetics and thus as a forerunner of physical organic chemistry. The year 1887, with Ostwald's founding physical chemistry in that year, came too close to the year 1884: the kinetics of sucrose inversion 1884 paper became assimilated into physical chemistry, instead of being identified as one of the earliest interfaces between organic and physical chemistry.

Conclusion

This particular example brings up a first point, sometimes history serves as a pointer to the advancement of science. The past may be the best guide on how to orient one's research in the future.

Another point is the masking of Ostwald's role as a pioneer of physical organic chemistry. Since, in the late 1880s, he was the inventor of physical chemistry as a discipline, it eclipsed his early contributions in defining physical organic chemistry in its aims and methods. A road sign used to be ubiquitous at railroad crossings in France: beware, a train can hide another. Likewise, the birth of a subdiscipline can hide another!

My final point, one that I have tried repeatedly to stress, is that often chemical history makes sense only in the long haul, the *longue durée* of Fernand Braudel.⁴² Only by enlarging the temporal scope can one understand properly the events and the attendant evolution.

References

- ¹ K. Leffek, *Sir Christopher Ingold: A Major Prophet of Organic Chemistry*, (Victoria BC: Nova Lion Press, 1996).
- ² J. Shorter, "Electronic theories of organic chemistry: Robinson and Ingold," *Natural Products Research* 4 (1987): 61-66.
- ³ P. Laszlo, "Features of mechanistic organic chemistry already present in 1910," *Ambix* 50 (2003): 261-73.
- ⁴ J. Shorter, *Correlation Analysis in Organic Chemistry: An Introduction to Linear Free-Energy Relationships*, (Oxford: Clarendon Press, 1973).
- ⁵ N. B. Chapman and J. Shorter, *Correlation Analysis in Chemistry*, Plenum Press, 1978).
- ⁶ R. I. Zalewski, T. M. Krygowski and J. Shorter, eds. *Similarity Models in Organic Chemistry, Biochemistry and Related Fields*. (Amsterdam: Elsevier, 1991).
- ⁷ A. Williams, *Free Energy Relationships in Organic and Bioorganic Chemistry*, (London: Royal Society of Chemistry, 2003).
- ⁸ W. Ostwald, "Studien zur chemischen Dynamik. III. Die Inversion des Rohrzuckers." *J. Prakt. Chemie* 29 (1884): 385-408.
- ⁹ J.-B. Biot, *Mém. Acad. Sci.* 13 (1835): 39-175.
- ¹⁰ M. Berthelot, "Sur la fermentation glucosique du sucre de canne," *Compt. Rend. Ac. Sci. Paris* 50 (1860): 980-84; see also C. O'Sullivan and F.W. Thompson. "Invertase: A Contribution to the History of an Enzyme or Unorganized Ferment." *J. Chem. Soc.* 57 (1890): 834-931.
- ¹¹ L. Michaelis and M. Menten, "Die Kinetik der Invertinwirkung," *Biochem. Z.* 49 (1913): 333-69.
- ¹² J. R. Partington, "Polarimeter," in *An Advanced Treatise on Physical Chemistry*, ed. J. R. Partington (London: Longmans, 1953), 347-53; S. F. Johnston, "Polarimeter, Chemical," in *Instruments of Science. An Historical Encyclopedia.*, ed. R. Bud and D. J. Warner (London: The Science Museum, 1998), 473-75.
- ¹³ P. Brenni, "Soleil-Duboscq-Pellin: A Dynasty of 19th century Scientific Instrument Makers," Eleventh International Scientific Instrument Symposium, Bologna University, 9-14 September; P. Brenni, "19th Century French Scientific Instrument Makers. XIII: Soleil, Duboscq, and Their Successors," *Bulletin of the Scientific Instrument Society* 51 (1996): 7-16.

- ¹⁴ Ward, R. "The Development of the Polarimeter in Relation to Problems in Pure and Applied Chemistry: An Aspect of 19th-Century Scientific Instrumentation." Ph. D. dissertation, London University, UK, 1979.
- ¹⁵ L. Laurent, "Sur le saccharimètre Laurent.," *Compt. Rend. Ac. Sci. Fr.* 89 (1879): 665-66.
- ¹⁶ Circumstances Ostwald was well aware of: see W. Ostwald, *L'évolution d'une science, la chimie*, (Paris: E. Flammarion, 1910), p. 255.
- ¹⁷ L. F. Wilhelmy, "Ueber das Gesetz, nach welchem die Einwirkung der Säuren auf den Rohrzucker stattfindet.," *Annalen der Physik und Chemie* 81 (1850): 413-28, 99-526, 27-32.
- ¹⁸ C. M. Gulberg and P. Waage, "Studier over affinitet. I-III.," *Forhandlinger I Videnskabselskabet I Christiania* (1864): 35-45, 92-94, 111-20.
- ¹⁹ J. W. Servos, *Physical Chemistry from Ostwald to Pauling: the Making of a Science in America*, (Princeton, NJ: Princeton University Press, 1990).
- ²⁰ S. Arrhenius, "On the Reaction Velocity of the Inversion of Cane Sugar by Acids," *Zeitschrift für Physikalische Chemie* 4 (1889): 226.
- ²¹ J. Walker, *Introduction to Physical Chemistry*, (London: Macmillan, 1899).
- ²² F. P. Worley, "Studies of the processes operative in solution XXII.," *Proc. Royal Soc.* 87A (1912): 563-81.
- ²³ E. W. Washburn, *An Introduction to the Principles of Physical Chemistry from the standpoint of modern atomistics and thermodynamics. A course of instruction for students intending to enter physics or chemistry as a profession.* (New York: McGraw-Hill, 1915).
- ²⁴ L. J. Curtis, "Concept of the Exponential Decay Law Prior to 1900," *American Journal of Physics* 46 (1978): 896-905.
- ²⁵ G. Rolfe, *The Polariscope in the Chemical Laboratory*, (New York: Macmillan, 1905).
- ²⁶ E. B. R. Prideaux, *Problems in Physical Chemistry with Practical Applications*, (London: Constable & Company, 1920).
- ²⁷ J. F. Spencer, *An Experimental Course of Physical Chemistry. Part II Dynamical Experiments.*, (London: G. Bell and Sons, 1921).
- ²⁸ A. Findlay, *Practical Physical Chemistry*, (London: Longmans, Green and Co., 1925).
- ²⁹ E. Mack and W. France, *A Laboratory Manual of Elementary Physical Chemistry*, (New York: Van Nostrand, 1928); E. Mack and W. G. France, *A Laboratory Manual of Elementary Physical Chemistry*, (New York: D. Van Nostrand, 1934).
- ³⁰ F. Daniels, J. H. Mathews and J. W. Williams, *Experimental Physical Chemistry*, (New York: McGraw-Hill, 1929); F. Daniels, J. H. Mathews and J. W. Williams, *Experimental Physical Chemistry*, (New York: McGraw-Hill, 1934); F. Daniels, R. A. Alberty, J. W. Williams, C. D. Cornwell, P. Bender and J. E. Harriman, *Experimental Physical Chemistry*, (New York: McGraw-Hill, 1970), Experiment 24, "Inversion of Sucrose".
- ³¹ J. R. Mohrig and D. C. Neckers, *Laboratory Experiments in Organic Chemistry*, (New York: D. Van Nostrand, 1973).
- ³² J. G. Dawber, R. R. Brown and R. A. Reed, "Acid-catalyzed hydrolysis of sucrose. A student study of a reaction mechanism," *Journal of Chemical Education* 43 (1966): 34.
- ³³ T. J. Zielinski and R. W. Schwenz, "Physical Chemistry: A Curriculum for 2004 and Beyond," *The Chemical Educator* 9 (2004):
- ³⁴ W. J. Wienen and R. S. Shallenberger, "Influence of acid and temperature on the rate of inversion of sucrose," *Food Chemistry* 29 (1988): 51-55.
- ³⁵ R. S. Dordick and G. A. Clarke, "Salt effects on the hydrolysis of sucrose," *Journal of Chemical Education* 56 (1979): 352.

- ³⁶ E. Y. Shalaev, Q. Lu, M. Shalaeva and G. Zografi, "Acid-Catalyzed Inversion of Sucrose in the Amorphous State at Very Low Levels of Residual Water," *Pharmaceutical Research* 17 (2000): 366-70.
- ³⁷ M. A. Gibas, "A polarimeter experiment for introductory courses.," *Journal of Chemical Education* 53 (1976): 462.
- ³⁸ M. D. Mosher, C. O. Kelly and M. W. Mosher, "Examination of a Reaction Mechanism by Polarimetry: An Experiment for the Undergraduate Organic Chemistry Laboratory," *Journal of Chemical Education* 73 (1996): 567-68.
- ³⁹ H. Klostergaard, "Inversion of sucrose and fructose structure," *Journal of Chemical Education* 53 (1976): 298.
- ⁴⁰ S. M. Mahurin, R. N. Compton and R. N. Zare, "Demonstration of optical rotatory dispersion of sucrose," *Journal of Chemical Education* 76 (1999): 1234.
- ⁴¹ D. P. Shoemaker, C. W. Garland and J. W. Nibler, *Experiments in Physical Chemistry*, (Boston: McGraw-Hill, 1996), 264-75.
- ⁴² F. Braudel, "History and the Social Sciences: *The longue durée*," in *Economy and Society in Early Modern Europe*, ed. P. Burke (London: Routledge and Kegan Paul, 1972), 11-42.