CHEMICAL GENEALOGY FOR PROFESSOR ROGER ATKINSON

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Introduction

So very difficult a matter is it to trace and find out the truth of anything by history.
Plutarch (46 AD-120 AD) in Life of Pericles.

Plutarch makes a valid point. Any one version of history is certainly going to be biased by the one reporting it. However, we attempt to do our best in the efforts that follow.

On this occasion, when Professor Roger Atkinson is receiving the American Chemical Society's Award for Creative Advances in Environmental Science and Technology, we felt it appropriate to explore his academic past, specifically his chemical genealogy. It is our premise that our past mentors contribute to our work in ways of which we might be unaware. The mentors' influence on generations of students perpetuates the mentors' experience and enthusiasm, invariably along with the keys to future creativity. We will briefly review some of Roger's past accomplishments and scientific interests, then continue back in time from mentor to mentor, briefly examining each individual's interests and accomplishments. We will look for similarities through time, highlighting areas of environmental and atmospheric chemistry.

Roger Atkinson (1945-) Ph.D. Chemistry, Cambridge, 1969

Roger obtained his doctorate in physical chemistry from the University of Cambridge in 1969, after obtaining his B.A. degree from that same hallowed institution in 1966. His thesis mentor was Professor Brian A. Thrush. Roger's interests then, as now, were focused on the kinetics and mechanisms of gas-phase reactions of atmospheric interest, particularly radical and atomic reactions with organic compounds.

One of us (J.S. Gaffney) first worked with Roger after he had completed postdoctoral appointments, one at the National Research Council in Ottawa, Canada, working with R.J. Cvetanovic, and another at York University. Roger joined the group of James N. Pitts, Jr., in 1972 and began studies on oxygen atom and OH radical kinetics. Recently we put together a chemical genealogy for Pitts (*1*).

Roger's guidance, along with that of Pitts, led to Gaffney's thesis work (*2-4*) and also aided in the earlier thesis work of Barbara Finlayson-Pitts (*5*). Roger's experience and abilities were very welcome by the Pitts group. Gaffney was particularly fortunate that Roger became a member of the hν crew (the name Pitts gave the research group), as he was working on reactions of ground-state oxygen atoms with organics, and Cvetanovic's group had a great deal of experience with that chemistry. Gaffney had done some product analyses on the reactions of $O(^3P)$ with toluene and benzene and an analog — 1-methylcyclohexene — and had found evidence of ring opening. With Roger's help and guidance, Gaffney learned about the use of relative rate methods for $O(^3P)$ reactions and the use of ethene formation from cyclopentene reaction, with the atom developed earlier in the Canadian research group's facilities. Three papers in the *Journal of the American Chemical Society* followed (*2-4*), as well as a doctorate for Gaffney in 1975.

Roger established the University of California, Riverside (UCR), as one of the leading institutions in the determination of OH reaction rates. His initial work was done in conjunction with D. Alan Hansen and Pitts in the chemistry department at that institution. He also worked closely with Alan C. Lloyd and William Carter on development of reaction kinetic models for air pollution modeling. In 1978, Roger left UCR to join Shell Research Limited in the United Kingdom. He returned to the United States in 1978, working with the firm Environmental Research and Technology (ERT) for a year before he returned to UCR in 1990 and became a research chemist and professor in soils and environmental science with a joint appointment in

chemistry. He is currently the director of UCR Air Pollution Research Center, where he and his wife, Dr. Janet Arey, continue laboratory work with others (e.g., Ernesto Tuazon) to unravel the oxidations of organic species important in the chemistry of the troposphere.

Roger has also done substantial theoretical work on structure and reactivity relationships. During the many discussions that Roger and Gaffney had in 1972-1975 on the reactions of oxygen atoms and OH radicals, the notion of using ionization potentials, bond-dissociation energies, and other physical constants to "predict" rates of reactions led to a number of papers in the area of structure-reactivity relationships. One of the initial papers led to comments (*6*-*8*) and continued work in the area by Roger and Eric Kwok. Roger's expertise in the area of kinetics and mechanisms has led him to do critical reviews of the rate constants for a number of key atmospheric species. Indeed, Roger is one of the 100 most cited chemists in the world, as noted by the Institute for Scientific Information. This achievement is due not only to Roger's productivity but also to the quality of his work throughout his career.

Thus, Roger's interests center on atmospheric chemistry, particularly the kinetics and mechanisms of reactions involving organic molecules. With that in mind, we now begin to examine the previous mentors in Roger's chemical genealogy, beginning with the 20th century mentors and his thesis mentor at Cambridge University, Professor Brian A. Thrush.

The Twentieth Century Mentors

Brian A. Thrush (1928-), Ph.D. Physical Chemistry, Cambridge, 1953; R.G.W. Norrish, Thesis Mentor

Thrush is a very well known, highly respected physical chemist and professor at the University of Cambridge. He has been a member of the Royal Society of Chemistry since 1950 and became a member of the Royal Society in 1976. He has served as editor for the *International Review in Physical Chemistry* since 1981 and as an associate editor for *Chemical Physics Letters* since 1971. His research interests and group have focused on the spectroscopy and reaction kinetics of atmospheric species.

Thrush began his thesis research in October of 1949, working with T.M. Sugden in the Chemistry Department. In January of 1951, Thrush's interests in spectroscopy and in fast kinetics led him to change mentors. He completed his thesis with Professor Ronald George Wreyford Norrish in 1953 (*9*). This was not a bad turn of events, as Norrish would later be awarded the Nobel Prize in Chemistry for his work in this area. Thus, Roger's interests were clearly well served by the training he received from Thrush.

Further exploration into Roger's chemical genealogy will find many other similarities in interests among past mentors (*10*).

Ronald George Wreyford Norrish (1897-1978), Ph.D., Cambridge, 1924; Eric Keightley Rideal, Thesis Mentor

Norrish is best known for his work on the development and application of flash photolysis. This work enabled exploration of the spectroscopy and kinetics of many short-lived species and gained Norrish the Nobel Prize in Chemistry, which he shared with one of his students, George Porter. Many consider Norrish one of the founders of modern photochemistry, and one photochemical reaction bears his name — the Norrish Type II photodissociation of long-chain ketones containing a gamma-hydrogen to a lower ketone and an olefin. Norrish was very interested in the kinetics of chain reactions, particularly as they related to combustion and polymerization. His classic studies of nitrogen dioxide, an important species in photochemical air pollution, demonstrated that photodecomposition did not occur until the absorption spectrum stopped showing any fine structure. His research group also showed that fluorescence ceased when photolysis began to occur. This work certainly influenced Thrush and other students, who went on to study the photochemistry, kinetics, and spectroscopy of many organic molecules.

Eric Keightley Rideal (1890-1974), Ph.D., Bonn, 1912; Richard Carl Johann Philipp Noe Anschutz, Thesis Mentor

Rideal was born the son of a public analyst and consulting chemist at Sydenham, Kent. In 1907 he entered Cambridge to study the natural sciences. A lecturer at Cambridge, Sir William Bate Hardy, introduced Rideal to surface chemistry, within which area he decided to focus on colloids and the kinetics of surface reactions. This led him to research work at Aachen and Bonn, Germany. Rideal obtained his Ph.D. in Bonn under the direction of Anschutz and co-wrote with H.S. Taylor the widely read *Catalysis in Theory and Practice*. We were interested to find that Rideal also was a visiting professor at the University of Illinois in 1919 and in 1921 (as Argonne National Laboratory is located in Illinois and has ties to the University of Illinois and to the University of Chicago). A fellow of the Royal Society and professor of colloid physics (colloid science) at Cambridge, he became interested in explosives, fuels, and polymers during World War II — which likely influenced Norrish in his interests. In 1946 Rideal left Cambridge to become the Fullerian professor of chemistry and director of the Davy-Faraday Research Laboratory at The Royal Institution of Great Britain. In 1949 he became professor of chemistry at King's College in London, and in the following year he was knighted. Sir Eric Rideal also was awarded the Davy Medal of the Royal Society in 1951.

The Nineteenth Century Mentors

Richard Carl Johann Philipp Noe Anschutz (1852-1937), Ph.D. Heidelberg, 1874; Freidrich August Kekule, Mentor

Anschutz was an organic chemist and a pioneer in vacuum distillation as a means of separation. He studied the chemistry of unsaturated diacids, particularly oxalic acid. He synthesized anthracene and studied effects of aluminum chloride in reactions involving shifts of alkyl side chains on substituted benzenes. Anschutz discovered a chloroform salicylide salt that was one-third $CHCl_3$ by weight and could be used as a source of high-purity chloroform for narcosis; the salt was given his name, Anschutz. His studies in Heidelberg followed attendance at lectures by Robert Bunsen (Bunsen burner) and Kirchoff in Berlin. Anschutz obtained his Ph.D. without dong laboratory work and then became Kekule's assistant. It was Kekule who became Anschutz's inspiration and who had the greatest influence on him and his career.

Friedrich August Kekule (1829-1896), Ph.D., Giessen, 1852; Heinrich Will, Thesis Mentor

Kekule was a very well known organic chemist who co-founded the structural organic chemical approach. His famous dream of a snake eating its tail led to his proposal of the correct structure for benzene. He introduced the concept of resonance and the tetravalent carbon atom. He correctly described the existence of doubly and triply bonded carbon atoms and concluded that in hydrocarbons the carbon atoms are bonded to each other. This led to his development of the 2n + 2 rule for alkane stoichiometry. Kekule studied the chemistry of organic acids and of azo and diazo compounds, as well as the carboxylation reactions of aromatic bromine compounds.

Heinrich Will (1812-1890), Ph.D., Giessen, 1839; Justus Von Liebig, Thesis Mentor

Will was the co-inventor of an improved method for nitrogen determination in organic compounds. His method led to the discovery of trinitroresorcinol and the discovery that mustard oil was an allyl thiocyanate compound. Will also was interested in vapor pressure measurements and invented a method for determining molecular weights on the basis of vapor pressure.

Justus Von Liebig (1803-1873), Ph.D., Erlangen, 1822; Karl Friedrich Wilhelm Gottlob Kastner, Thesis Mentor

One of the great chemistry teachers of the 19th century, Liebig learned organic chemistry from Joseph Louis Gay-Lussac. Gay-Lussac was very interested in the chemistry of gases and the composition of the atmosphere. Indeed, Gay-Lussac at one point held the world record for a balloon ascent (7,019 meters)

during which he collected air samples. Liebig's degree came from his studies with Kastner, but much of his organic chemistry knowledge came from Gay-Lussac. Liebig studied metabolism and concluded that the process was due to the oxidation of food. He discovered structural isomers and proposed functional groups as a concept in organic chemistry. He was very interested in combustion chemistry and devised methods to identify the chemicals produced by combustion. He also studied the role of fertilizers in the growth of plants and was a pioneer in agricultural and food chemistry.

Karl Friedrich Wilhelm Gottlob Kastner (1783-1857), Ph.D., Jena, 1805; Johann Friedrich August Gottling, Thesis Mentor

Kastner was a very prolific writer and a man for all seasons. He was a pharmacist, chemist, teacher, and author. He wrote textbooks on industry, chemistry, and meteorology. He was very interested in triboluminescence, the emission of light when a crystal is sublimated or dissolved or physically crushed. Kastner studied the catalytic effect of platinum metal on the combustion of hydrogen and invented a galvinometer. He also developed a number of methods for water purification and analysis.

One can readily see that many of the 19th century mentors were interested in organic chemistry, in the mechanisms of reactions leading to the emission of light, and in the chemistry of combustion processes. Also note that many of them were interested in or associated with scientists involved in the study of the atmosphere around them.

The Eighteenth Century Mentors

Johann Friedrich August Gottling (1753-1809), Apothecary, Langensalza, 1775; Johann Christian Wiegleb, Mentor

Gottling was known for his studies on the chemistry of sulfur, arsenic, phosphorus, and mercury. He wrote a text on analytical chemistry, and he developed and sold chemical kits to determine sugar yields in beets as a means to supplement his very meager salary at the university. He studied the oxidation reactions of organic compounds with nitric acid as the oxidant (another nitrogen oxide product and an air pollutant). Gottling was among the first to embrace the new chemistry proposed by Lavoisier in France.

Johann Christian Wiegleb (1732-1800), Apothecary, Langensalza, circa 1765; Ernst Gottfried Baldinger, Mentor

A phloginist and apothecary, Wiegleb founded the first chemical and pharmaceutical institute in Germany. He studied many diverse systems from fermentation to the combustion of chalk and was the first to report that oxalic acid was a separate compound. Wiegleb was first apprenticed to Sartorius in Dresden but really began his chemistry studies with Baldinger in 1755. He isolated alkaline salts from plants and disputed the possibilities of element transmutation.

Ernst Gottfried Baldinger (1738-1804), M.D., Jena, 1760; Christoph Andreas Mangold, Thesis Mentor

Baldinger was a medical professor who founded a chemical laboratory at Marburg. He was noted for having established the first specialized scientific journal, *Magazine fur Artze*, in 1775. He also wrote a notable textbook on the ailments of soldiers based on his experiences as a battlefield surgeon during the Seven Years' War.

Christoph Andreas Mangold (1719-1767), M.D., Erfurt, 1751; Georg Erhardt Hamberger, Thesis Mentor

Mangold was a professor of philosophy and anatomy, as well as chemistry. He was very interested in the chemistry of gunpowder and was one of the first to analyze cinnabar. His background and interests led him to propose a new system for medical practice based on the idea that diagnosis should only be made after comparison of the patient's symptoms and tests with those of previously studied patients. He was a pioneer in trying to understand the underlying mechanisms that caused illnesses and complications, noting that a

therapy must be judged thoroughly and not considered effective just because symptoms are relieved or the patient improves, as many patients will get well on their own regardless of the therapy.

Georg Erhardt Hamberger (1697-1755), M.D., Jena, 1721; Johann Adolph Wedel, Thesis Mentor

Hamberger was a professor of botany, surgery, and medicine. He was especially interested in the physiology of respiration and the mechanism of breathing. He authored an important book on the function of the thorax, the intercostal muscles, and the pleural sac in the physiology of respiration. He wrote a number of texts on gravitation and the ascension of gases. We again note an interest in the physics of the atmosphere and its mechanisms in this mentor during the 18th century. Hamberger also examined the oxidation of camphor by nitric acid.

The Seventeenth Century Mentors

Johann Adolph Wedel (1675-1747), M.D., Jena, 1697; Georg Wolfgang Wedel, Thesis Mentor

J.A. Wedel was a professor of medicine who was very interested in the processes of fermentation and the combustion of sulfur (another air pollutant). He published a number of textbooks on these subjects, the chemistry of camphor and magnesium carbonate, and medical topics.

Georg Wolfgang Wedel (1645-1721), M.D., Jena, 1669; Werner Rolfnick, Thesis Mentor

G.W. Wedel was a professor of botany, practical medicine, theoretical medicine, surgery, and chemistry. He also was a prolific author who focused on alchemy and pharmaceutical chemistry. He studied volatile salts obtained from plant extracts, invented many new medicines, studied copper plating from sulfate solutions, and — in his spare time — translated a new edition of the Greek Bible into his native German language.

Werner Rolfnick (1599-1673), M.D., Padua, 1625; Adriaan van den Spieghel, Thesis Mentor

Rolfnick was the first chemistry professor at the University of Jena. He also was a professor of anatomy, botany, and surgery. In his lectures he used the corpses of executed criminals for dissection, an innovative approach that aroused some controversy and some criticism. He was the first physician to demonstrate the location of cataracts in the lens of the eye. He was an adamant critic of the alchemical and superstitious thinking that abounded during his time, and he wrote a number of texts on the impossibility that chemical treatments could lead to the transmutation of lead to gold, the resuscitation of plants from ashes, the production of oils from precious stones, and other common folklore of the period. Rolfnick also wrote a number of influential texts on pharmaceutical chemistry.

Adriaan van den Spieghel (1578-1625), M.D., circa 1603; Girolamo Fabrici and Giulio Cesare Casseri, Mentors

Another of the Paduan medical heritage, Spieghel was a professor of anatomy, botany, and surgery. He published one of the first texts on plant anatomy, a book on human embryology, and an influential posthumous anatomy, *De Humani Corporis Fabrica*. He studied with both Fabrici and Fabrici's student Casseri.

The 17th century mentors were primarily physicians and chemists who were interested in the workings of plants and animals. Again, trying to understand the mechanisms of how things worked was at the heart of their studies and interests.

The Sixteenth Century Mentors

Giulio Cesare Casseri (1552-1616), M.D., Padua, 1580; Girolamo Fabrici, Thesis Mentor

Casseri's main claim to fame was his investigations into the organs of speech and hearing. He is especially noted for his identification of the tympanic nerve and its relationship to the hammer and stirrup bones of the ear. His work was published with extensive anatomical tables, showing a great deal of patience and attention to detail. He was a professor of surgery and anatomy.

Girolamo Fabrici (Aquapendente) (1533-1619), M.D., Padua, 1559; Gabriele Fallopio, Thesis Mentor.

Fabrici was the teacher of William Harvey, who is credited with the discovery of the blood circulation in the human body. Fabrici was a professor of anatomy and surgery. He described in detail the valves in veins and wrote anatomy texts on the larynx, the lens of the eye, the mechanisms of respiration, and the actions of muscles. He was the first to publish an exhaustive study on chick embryos, thus establishing the fields of comparative and developmental embryology in the 16th century.

Gabriele Fallopio (1523-1562), M.D., Ferrara, 1548; Antonio Musa Brasavola, Thesis Mentor

Fallopio was a professor of botany, anatomy, and surgery who discovered the Fallopian tubes and described the anatomy of the kidneys. He also focused on the human skull and its structure, particularly the facial and cranial nervous system. Fallopio also studied the ossification of bones and teeth during growth and was the first to describe the cochlea, vestibules, and semicircular ear canals. He was a colleague of Andreas Vesalius, the publisher of the first complete human anatomy.

Antonio Musa Brasavola (1500-1555), M.D./Ph.D., Ferrara, 1520; Nicolo da Lonigo, Thesis Mentor

Brasavola was physician to crowned heads of Europe including Francis I of France, Kaiser Charles V of Germany, and King Henry VIII of England. He also attended Popes Paul III, Leo X, Clemens VII, and Julius III. Brasavola developed medicinal applications for plants and herbs, was the organizer of the famous botanical gardens of Belvedere, and published a summary of Galen's writings.

The Fifteenth Century Mentors

Nicolo da Lonigo (Leoniceno) (1428-1524), M.D., Padua, 1453; Pelope, Mentor

Lonigo was a professor of mathematics, Greek philosophy, and medicine. He was largely responsible for the reformation in medicine that occurred during the 16th century. Lonigo's accurate translations of ancient Greek texts, particularly those of Galen and Hippocrates, into Latin aided in this accomplishment. He published the first scholarly work on the spread of syphilis, which in his time had only recently appeared in Europe. Lonigo is one of the most famous scholars of his time.

Pelope

With Pelope the trail back in time ends. Little is known about Pelope, except that he was the teacher of Nicolo da Lonigo.

Some Final Remarks

Looking back through the past clearly shows that many of Roger Atkinson's mentors passed on key ingredients of a successful scientific career. These ingredients are simply the desire to understand the mechanisms and processes of the world around us, the ability to examine systems with patience and attention to detail, and the ability to interpret observations in a way that leads to a better working understanding of a system. Roger Atkinson's chemical genealogy is an impressive one. From Nobel

Laureates in the 20th century to leaders of the reformation in medicine in the 15th century, the mentors have passed on their interests and enthusiasm for determining how things work. As we recognize Roger for his work in atmospheric chemistry and chemical mechanisms, let us look forward to the future as Roger's students and colleagues continue to explore the world around us at the molecular level.

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