Frederic Stanley Kipping—Pioneer in Silicon Chemistry: His Life & Legacy

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Received: 6 April 2010 / Accepted: 26 July 2010 / Published online: 12 August 2010
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Abstract Frederic Stanley Kipping FRS is regarded as one of the founding fathers of silicon chemistry. In 57 research papers published between 1899 and 1944 he reported the first use of Grignard reagents to make alkylsilanes and arylsilanes and the preparation of silicone oligomers and polymers. He coined the term ‘silicone’ in relation to these materials in 1904. His research formed the foundation for James Franklyn Hyde’s development of the first silicon based insulation materials at Corning Glass Works and then Dow Corning Corp., as well as inspiring Eugene G. Rochow’s work at General Electric Company in the development of the ‘direct method’ of silicone synthesis using silicon hydrides. Kipping was the first Sir Jesse Boot Professor of Chemistry at Nottingham University College and was married to Lily Holland whose sisters, Mina and Kathleen were married to two other prominent early 20th century British Chemists, William H. Perkin Jr. FRS and Arthur Lapworth FRS. This paper provides an insight into Professor Kipping’s life, personality and career.

Keywords Kipping · Silicon · Silicone · Holland · Perkin · Lapworth · Nottingham · Hyde · Rochow

During a visit to the UK in 1945 Dr Shailer L. Bass, then director of research at the recently formed Dow Corning Corp. (1st April 1942) and later (1967) CEO and board chairman of the company, called on Prof. Frederic S. Kipping who at that time was living in Criccieth, Wales (Fig. 1). It is

alleged that Dr Bass said “You know, it was you and Mr Churchill that won WW2”, Kipping’s sharp response was “Why bring Churchill into it?” The basis for this comment comes from developments a few years earlier when the Dow Chemical Company (supplying magnesium) had entered a joint venture with Corning Glass Works in Midland, Michigan to form the Dow Corning Corporation to produce products based on new materials called silicones. This built on the promising results of one of the Corning scientists James Franklin Hyde who combined glass fibres with ethylphenyl-silicone produced by a method originally developed by Kipping to give a good insulating material. One of the first commercial uses of these products was a silicone grease developed by Shailer in 1942 (Dow Corning® 4 compound) to protect aircraft ignition systems from corona discharges which occurred with other insulators employed at the time such as shellac. Using Dow Corning® 4 compound in the sparkplug boots and electrical harnesses allowed aircraft to remain at 35,000 ft for up to 8 h and hence be flown directly to the UK and North Africa instead of being transported by ship. This significantly reduced the risk of them being destroyed by Axis forces and speeded up supply. A further reference to the crucial use of silicones during WW2 is given in the journal Chemical and Metallurgical Engineering in August 1944:

[the] most propitious single wartime development in the entire resins and plastics field is the recent commercialization of the silicone series of resins by Dow Corning Corporation [1].

Much of the underpinning research on organosilicon chemistry that led to these developments was conducted by Kipping, who between the years 1899 and 1944 published 57 papers on silicon chemistry. He initially used silicon tetrachloride and alkylzinc reagents [2] and then the Wurtz-Fittig reaction with silicon tetrachloride and alkylhalides or

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Fig. 1 Kipping with Dr Shailer L. Bass of the Dow Corning Corporation during the visit of the latter to Criccieth, North Wales in November 1945 (Courtesy of the Dow Corning Corporation)

arylhalides and sodium metal [3] to generate the silicols (silanols) and silicanes (silanes), before pioneering the use of the then newly discovered Grignard reagents to prepare these compounds (Scheme 1) [4]. The first silicone polymers were reported in 1904 and characterised as “sticky messes of no particular use” by Kipping. These were small oligomers produced from the dehydration of silanediols (Scheme 2). The term “silicone” was first used by Friedrich Wöhler in 1857 to describe chemicals now known as cyclic polysilanes, persilacycloalkanes or siloxanes with six membered rings composed solely of silicon [5]. However it is now widely used for the meaning Kipping gave to it in papers on the hydrolysis products formed with disubstituted silicon chlorides for compounds (silanones) that had an empirical formula of “RR'SiO” in an analogy to organic ketones of formula RR'CO, where R and R' are organic groups [6]. Chemically, silicones bear little resemblance to ketones, however, and only exist in isolable form as oligomers and polymers monomeric (silanones have been detected in the gas phase and in glasses by IR spectroscopy), the differences between these two types of compounds also illustrate a fundamental difference between silicon and carbon chemistry as later acknowledged by Kipping. Further to this, Kipping was one of several people who proposed a general systematic nomenclature for alkyl and arylsilicon derivatives, in his case based around the term

‘silicane’ [7, 8]. However, this was thought too unwieldy and was soon replaced by the term silane that is now in common usage.

Frederic Stanley Kipping was born on 16th August 1863 at Higher Broughton near Manchester and lived most of his early life in the Manchester area. He went to Manchester Grammar School doing vacation work for Mr Carter Bell, the public analyst for Cheshire. During this period he also spent a year at a Lycee in Caen, France. He then read Zoology at Owens College (now Manchester University) obtaining a second class BSc degree in Zoology in 1882 which was accredited by the University of London. He specialised in this area rather than Chemistry as he found the teaching style of Prof. Carl Schorlemmer (known as the ‘Red’ Chemist because of his friendship with Karl Marx and Friedrich Engels) [9, 10] to be rather dry, preferring to spend his time at the billiard table in a local hotel during these lectures. Kipping was an active sportsman also playing ‘Fives’ (a type of hand-tennis), lacrosse and cricket. Following this he took up a position at the Manchester Corporation Gas works in Rochdale Road, and later Gaythorne Street, Manchester, but quickly became aware that the job was undemanding and with little opportunity for advancement. Much of his free time was spent playing tennis at a good amateur level for the Northern Lawn Tennis Club.

In 1886 on the advice of a family friend, Dr Adolf Liebman, a chemist at the dye manufacturers Levinstein's, Kipping took up a position in Adolf Von Baeyer's Institute, at the University of Munich. Here he was supervised by William H. Perkin, Jr (son of Sir William Henry Perkin, the discoverer of mauveine dye that initiated the development of the aniline dye industry) [11, 12] who had entered the institute in 1882. Claisen, Bamberger and von Pechmann were *privat-dozenten* and Nef was a student in the lab at this time. Kipping worked on his Ph.D. which was titled ‘The synthetical formation of closed carbon chains.’ In an interview for ‘The Gong’ the University College of Nottingham, student newspaper in January 1898 [13], Kipping reflected on his time in Germany and the difference between the two countries indicating that “*things are different in Germany. The Teutons (Germans) take their studies so much more seriously. The English student is at least as good material as the German, but*

Scheme 1 The synthesis of silanes using organozinc, Wurtz-Fittig and Grignard reagents

Scheme 2 The synthesis of silicones through the dehydration of silane diols (silicols)

our country won't recognise the necessity of prolonged application", this is exemplified by the difference in the length of study for University degrees which continued well into the twentieth century. "It is a common thing in Germany for a student to spend 10 years in preparation, whereas here 3 years is deemed ample. German fathers too, encourage their boys to remain at college as long as possible, while an Englishman sets his son at once to some wage-earning work, so that he can only prosecute his studies by means of painful and unsatisfactory night work." Kipping did find the working atmosphere reasonably congenial "Eight hours I think is about the maximum for most people. In Germany students work from eight in the morning to six at night, including two meals and unlimited beer and smoking". Perkin Jr. later took over as Prof. of Organic Chemistry at Owens College, Manchester in 1892 after the untimely death of Schorlemmer and Kipping commented on this that "Owens has changed greatly since Prof. Perkin (Jr.) took charge of the organic chemical department. Its organic laboratory can compare with those in Germany—a thing which can be said of few English laboratories".

On returning to the UK in 1887 having obtained a Ph.D. *summa cum laude* (München) and D.Sc. (London), Kipping initially worked with his father on small scale commercial chemical preparations in the stables of their house in Platt Abbey. However, he was soon appointed as a demonstrator at Heriot-Watt College, Edinburgh under Prof. W.H. Perkin, Jr. with a remuneration of £20 per year 'with prospects'! Prof. Perkin had been introduced to Mina Holland, one of Frederic Kipping's cousins whilst visiting Manchester during his Ph.D. and after several years and some urging from Kipping (as the eldest daughter was expected to marry first at the time), Perkin and Mina were married in Bridgwater, Somerset on New Year's eve 1887. Soon after Kipping married Lily Holland, Mina's younger sister at the same church on 3rd March 1888. Kipping had known Lily from when they were both young children and later they had often played mixed doubles tennis together, spending summers either in Bridgwater or Manchester. The Holland sisters were the grand daughters of a well known Manchester artist Charles Allen DuVal.¹

¹ For a semi-fictionalised account of the lives of the Holland sisters see [14].

Kipping was promoted to Assistant Professor of Chemistry and lecturer in Organic Chemistry at a salary of £150 per year, but the offer of a better paid position (£240 pa) as Chief demonstrator at the Central Technical College of the City and Guilds of London in Bloomsbury (later merged into Imperial College of Science and Technology) and the fact that London was much more convenient for visiting Lily's family caused them to move there in 1890, just after their first daughter Frieda was born. Kipping conducted research in the laboratory of Prof. H.E. Armstrong on the chemistry of camphor derivatives during this period and he was assisted by Arthur Lapworth. Some years later on 14th September 1900 and again at St Mary's Church, Bridgwater, Mina and Lily Holland's younger sister, Kathleen married Lapworth. He had been a demonstrator in the School of Pharmacy in Bloomsbury before moving to Goldsmiths Institute (1900) as head of Chemistry and then Senior Lecturer at the University of Manchester (1909) where he succeeded William H. Perkin Jr. becoming Professor of Organic Chemistry in 1913 [15] when the latter became Waynflete Professor of Chemistry at Oxford [16]. Lapworth is regarded as one of the pioneers of physical organic chemistry.

During this period together with William H. Perkin Jr., Kipping completed the first edition of the seminal textbook 'Organic Chemistry' (1894). New editions and revisions were produced for the next 45 years with the book being used well beyond the lifetime of both authors. In 1897 Kipping was elected a Fellow of the Royal Society at age of 34 and appointed Chair of Chemistry at University College, Nottingham in succession to one of the founding faculty of that institution, Prof. Frank Clowes. The Chemistry laboratories were located in the Arkwright Building, Shakespeare Street, sandwiched between the city library and city museum and opened in 1881 and extended in 1892 (Fig. 2). At the time Kipping joined the Department, it consisted of four full-time students working for associateship of the Institute of Chemistry. It was during this period that Kipping began his work on silicon compounds. Kipping built on his interest in stereochemistry of non-carbon centres, especially tetravalent nitrogen compounds with a number of papers in the period 1900–1905. He then turned his attention to the preparation of asymmetric silicon compounds, typically preparing aryl containing chiral silicon compounds and the converting them to their sulphonic

Fig. 2 The Arkwright Building, Shakespeare Street University College Nottingham, where Frederic Kipping's main laboratories were located from 1897–1928. This is now part of Nottingham-Trent University. Pictures from the 1890's and 2010

acids so that they could be resolved by crystallisation with the single enantiomer of a nitrogen containing cationic natural product such as brucine (Scheme 3). Between 1899 and 1944 Kipping produced 57 papers on silicon chemistry, 53 in the *Journal of the Chemical Society*, 3 in *Proceedings of the Chemical Society* and one in *Proceedings of the Royal Society, London*. These are tabulated and the chemistry reported is analysed in detail in these references [17–20].

The research fell into three main themes, the synthesis and resolution of asymmetric compounds of silicon which was the main focus of research until 1910—an example is shown in Scheme 3; the preparation of silicones/siloxanes through the condensation of $R_2Si(OH)_2$ and $RSi(OH)_3$ which involved much laborious separation of complex mixtures of oligomers to identify individual components (Scheme 2); and, thirdly the reactions of arylchlorosilanes with sodium. His work in these areas was recognised by the Longstaff medal of the Chemical Society of London in 1909 and the Davy medal of Royal Society of London in 1918. Through an endowment of £20,000 from Jesse Boot of Boots the Chemists, a company started in Nottingham in 1883, Kipping was appointed as the first Sir Jesse Boot Professor of Chemistry in 1920.

On moving to Nottingham, Kipping became a regular at the Nottingham Park Tennis Club as well as the Notts Golf Club in Hollinwell where he regularly played the linguist Prof. Ernest Weekley from 11 to 3 or 4 on a Wednesday. Prof. Weekley is perhaps best remembered because his wife Frieda (*nee* Baroness von Richthofen) eloped with one of his pupils, the author D.H. Lawrence in 1912.² Prof. Frederick Challenger, one of Kipping's students from

1908–1911 has commented that “*On Wednesdays.....his students felt secure from his severe and searching interrogations*” suggesting Kipping was a demanding and highly attentive supervisor.³ He expected a ‘exacting and severe standard of scientific accuracy at once the despair and the inspiration of his research students’. He encouraged them by saying “*You want to get up in the morning and think out ten times as much as it's possible to do, and then come down and do it*”. Kipping was extremely rigorous concerning the quality of products his researchers obtained “*If _____ says a substance is pure he means there's 50 per cent there and if he says it's crude then there's none there at all*”.

His acerbic wit is perhaps best illustrated from an example recalled again by Frederick Challenger: Whilst giving a lecture on minerals, a student added a bar of soap amongst the minerals. Kipping picked these up in turn—“*Here is a piece of calcite—calcium carbonate. Here is a piece of galena—lead sulfide*”. Picking up the soap—“*Here is a piece of impudence!*”

During the First World War Kipping's group was involved in the synthesis of aspirin and sulfa drugs that could not be obtained from the German drug industry. He was also involved in the training of the Officer Training Corp in both map reading and rifle shooting. The demand for higher education significantly increased in 1918 with the return of servicemen from the front and additional laboratory space was made available in the City Museum adjacent to Kipping's lab. Through the further philanthropic gift of Sir Jesse Boot (later Lord Trent), University College Nottingham was offered a new large campus in the western suburbs of the

² Letters mentioning Kipping and from Lily Holland to Frieda Weekley can be found in the Ransome collection at the University of Texas at Austin and in the Letters of D.H. Lawrence (8 volume set) [21].

³ Frederick Challenger; Transcribed from the audio recording of a lecture given by Prof. Challenger on Frederic Stanley Kipping in the early 1980's

Scheme 3 The resolution of asymmetric silanes through the formation of the monobenzyl sulphonic acid and crystallization with brucine

city in 1920 and Kipping was intimately involved in the planning and design of the new chemistry labs. The Trent building was opened by King George V in 1928 (Fig. 3). His work on silicon chemistry proceeded unabated for the next 8 years, until his request to retire was finally accepted by the college council at the age of 73 in 1936. The high regard he was held in by both staff and students was recognised by a dinner on 11th January 1936 (Fig. 4) organised to celebrate both his retirement and the publication of the 50th part of his Organic derivatives of silicon in the Journal of the Chemical Society [22]. This was followed by an invitation to deliver the Bakerian Lecture of the Royal Society in the summer of the same year [23]. He ended his presentation by stating that:

We have considered all the known types of organic derivatives of silicon and we see how few are their number in comparison with the purely organic compounds. Since the few which are known are very

limited in their reactions, the prospect of any immediate and important advance in this section of chemistry does not seem very hopeful.

Little did he appreciate that James Franklin Hyde at Corning Glass Works following Kipping's method of making chloro silanes with Grignard reagents and Eugene G. Rochow at General Electric Company (using a 'direct' synthesis of chlorosilanes involving a copper catalyst) would within a few years build on his research and realise that what Kipping thought were "sticky glue-like masses" of no importance could have significant value when combined with glass fibres or as lubricants to produce new compounds for uses such as the first class H insulators in electric engines and transformers, waterproof seals for sparkplugs in aircraft and later giving rise to an industry producing fluids, resins, elastomers, sealants, and silanes valued at more than \$8 billion per annum in 2000.

Fig. 3 (Top) The Trent Building, University Park where Frederic Stanley Kipping's main laboratories were located from 1928–1936. Picture from 1928. (Bottom) Kipping lecturing in the 1930's

Fig. 4 (Left) Record card produced by one of Kipping's students, Dr. N.W. Cusa and signed by all those in attendance at the dinner to celebrate Prof. Kipping's 50th paper on the Organic Derivatives of Silicon and his impending retirement. Note along with the normal laboratory paraphernalia, the crocodile refers to the space in the City Museum that Kipping's group took over after 1918 which was

occupied by stuffed animals. (Right, Top) Photograph of those attending the dinner. Frederic Stanley Kipping is 3rd from left in front row. (Right, Bottom) The Kipping and Lapworth Families in *Ca* 1930. Back Row. Peggy, Barry and Frieda Kipping, Arthur Lapworth, Arthur Scott, Kathleen Lapworth; Front Row: Lilly, Brian and Frederic Stanley Kipping, unknown

Kipping continued as an Emeritus Professor working in his old labs in Shakespeare Street, Nottingham until his concerns over the safety of his family from the impending hostilities in Europe caused him to move with his wife and youngest daughter to Cricketh, near Porthmadog in North Wales. No doubt he was also attracted by the local golf courses. As was observed by the Vice-Chancellor of Leeds "he owed his perennial youth in no small measure to...an expert manipulation of cyclic compounds on the golf course, the tennis court and in the billiard room".

During this period his advice was sought by researchers from Dow Corning Corporation and General Electric Company on the synthesis and properties of silicones and the War office also provided him with a number of assignments. He produced his final research paper in 1944, and his contribution to silicone chemistry was recognised by the visit of Dr Shailer L. Bass from Dow Corning in 1945, alluded to at the beginning of this article (Fig. 1). He brought with him a 3 volume collection of Kipping's collected papers on the Organic Chemistry of Silicon derivatives, retyped and printed on acid-free paper and bound with silicone resin impregnated

glass fibre boards. These now reside in the special collection of the University of Nottingham. The University was awarded its charter as an independent degree awarding institution in 1948. With the aid of his son, Frederic Barry Kipping, a lecturer in Chemistry at Cambridge who had taken over from William H. Perkin Jr. as co-author of Perkin and Kipping's Organic Chemistry on Perkin's death in 1928, a final edition of the textbook was published in 1950. After a short illness Kipping died on the 1st May 1949 at the age of 85.

In recognition of Frederic Stanley Kipping's contribution to silicon and especially silicone chemistry, the Frederic Stanley Kipping Award in Silicon Chemistry was established in 1960 by Dow Corning Corp. Fittingly Eugene G. Rochow, one of the pioneers of silicone chemistry was awarded the prize in 1965. The University of Nottingham also has a number of Kipping Awards made possible by a bequest from the Kipping estate to recognise excellent performance by undergraduate chemistry students. Prof. Eugene Rochow with the aid of Eduard Krahé and Brian Kipping produced a semi-fictional story of the lives of the Holland sisters, and their influence on their husbands,

Perkin Jr., Kipping and Lapworth [14]. Kipping's contribution to silicone chemistry has further been recognised during the Centenary year of his synthesis of the first silicone polymers by the award of a Royal Society of Chemistry Historic Chemical Landmark Plaque to the School of Chemistry at the University of Nottingham on 17th March 2004 [24] an event which was attended by Kipping's grandsons Brian and Robin Kipping. Kipping was also inducted into the International Rubber Hall of Fame, at the Goodyear Polymer Center at the University of Akron Ohio on 12th November 2004 [25].

Acknowledgements Dr Harold Booth, School of Chemistry, University of Nottingham Archivist for the provision of the audio recording of Frederick Challenger's lecture on Frederic Kipping and the record card and photograph of the attendees at the party to celebrate Kipping's 50th research paper on silicon chemistry, and the Dow Corning Corporation for permission to use the photograph of Kipping with Dr Shailer Bass.

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