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Professor Wolfgang Walter in memoriam

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Obituary

Professor Wolfgang Walter in memoriam

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One cannot think of organosulfur chemistry in Germany in the 20th century without considering the scientific contributions of Professor Wolfgang Walter, who passed away on March 29th, 2005 at the age of 85.

Wolfgang Walter, our Academic Supervisor (“Doktorvater”), was born on November 19th, 1919, in Hamburg, the “Free and Hanseatic City” on the banks of the Elbe river, for which he showed a life-long affection. He grew up there and went to school at the well-known “Kirchenpauer-Gymnasium”. Immediately after his graduation (“Abitur”) in 1938 he was drafted as soldier and experienced the Second World War until 1945. He had a narrow escape, but was heavily wounded.

Right after his return from war captivity he began to study chemistry in the winter term of 1945/46, when teaching started again at the University of Hamburg. He graduated as a “Diplom-Chemiker” in 1950 and was granted the degree “Dr. rer. nat.” in 1953 after only seven years of undergraduate and graduate studies.

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Being then a member of Kurt Heyns' group, his first scientific studies and his PhD thesis [1] were of course devoted to natural products chemistry, in particular to amino acid, peptide, and protein chemistry. Several papers appeared in the 1950s, which dealt for instance with the synthesis of amino acids [2] and their detection and identification in proteins [3]. In 1957, the famous experiments of S. Miller and H. C. Urey on the formation of organic compounds by electric discharges in atmospheres of simple gases were reproduced and confirmed in Hamburg. Not unexpectedly, Walter complemented the experiments by the addition of hydrogen sulfide to the gases [4].

At the same time, Walter published his first papers on quite differing topics, which are indicative of his early, but just as much his long-term interests in the chemistry of organosulfur compounds, especially from the perspective of physical organic chemistry. As early as 1953 he came across the problem of valence shell expansion of the sulfur atom, an issue which fascinated many sulfur chemists for decades and raised passionate debates on the participation of d-orbitals in reactions of organosulfur compounds [5].

In 1955, Fritz Arndt, one of the grand old men of organic chemistry, retired from the University of Istanbul, where he had lived in exile after being expelled from Nazi Germany. After an interlude in the USA, mostly at the Indiana University at Bloomington, IN, he returned to his native town Hamburg and was appointed Honorary Professor at this University. Naturally, Walter came to know him. He highly esteemed his fascinating personality and induced him to give lectures on physical organic chemistry, which at that time was far-sighted and very helpful for the students in Hamburg, one of the authors (JV) included, because of the urgent demand of modern science in postwar Germany. Walter and Arndt jointly published several papers on structural ("The Thiopin Problem") [6] and mechanistic problems [7]. Eventually, Walter wrote an obituary on Fritz Arndt [8], who had obviously stimulated his lifelong interest in the theoretical background of organic chemistry.

Proceeding from peptide, i.e. amide, chemistry, Walter started his investigations on thioamides, which became one of the most important topics of his scientific life's work. His experiments were first aimed at the oxidation products of the thioamides, the thioamide *S*-oxides—exotic species at that time. Although an early Japanese report [9] on "thioperimidic acids" (tautomers of the *S*-oxides) existed, Walter undoubtedly was the real pioneer to explore this class of compounds which, by the way, represented the first examples of stable sulfine-type thiocarbonyl oxides. First, the prototype thioacetamide *S*-oxide was studied and fully characterized in his "Habilitationsschrift" [10]. He published the results as "*Oxydationsprodukte von Thiocarbonsäureamiden, I. Thioacetamid-S-Oxyd*" [11]. In the following decades, numerous papers on the preparation, structural properties and chemical reactions of *S*-oxides of all types of thiocarbonyl compounds arose from the Hamburg laboratory. The investigations included not only the primary, secondary and tertiary thioamides in the true sense but also thiono and dithiocarbamates, thioureas, thiohydrazides, and thiosemicarbazides as well as enaminothiones and heterocycles with endocyclic thiocarbonyl functionalities. The series of these publications was finished in 1977 with the 42nd communication [12]. The exploration of the chemistry of thioamide *S*-oxides had then virtually reached a state of completion.

The comprehensive study of the oxidation reactions obviously required numerous syntheses of thioamides. In this connection also novel methods were developed. One of the most interesting and important ones consisted in the reaction of trichloromethane with sodium hydrogensulfide and amines which gave thioformamides via dichlorocarbene as intermediate [13]. This reaction not only represented a very elegant preparative method but also became the starting point for a new series of studies on "*The Structure of Thioamides and their Derivatives*" [14]. One of the products, *N*-benzyl-*N*-methyl-thioformamide, existed as two distinguishable isomers which could be shown to be *E/Z*-isomers. This was proved by use of ¹H NMR spectroscopy [15], the most powerful new tool which had just found its

first applications in organic chemistry. The crystalline isomer could be isolated from the mixture and was shown by an X-ray structural analysis to exhibit the *E*-configuration [16]. This rather unexpected result was of course due to the phenomenon of hindered internal rotation around the partial C,N-double bond, which is particularly pronounced in thioformamides [17]. As a consequence, Walter and his group started systematic investigations on this effect and on further topics related with the structure of thioamides and similar compounds including selenium derivatives. All types of physical methods, i.e. UV/VIS [18], IR [19, 20] Raman [20] ¹H [15, 21] and ¹³C NMR spectroscopy [22], X-ray crystallography [16, 23] as well as dipole moment [24] and MS measurements [25] were applied in his group. This series of publications ended in 1979 with its 42nd communication [26].

Naturally, Walter's studies in the field of organosulfur chemistry were by no means confined to oxidation reactions and structural properties of the thioamides. Rather, their reactivity was explored comprehensively. Publications on alkylation [27], acylation [28], silylation [29], electrophilic amination [30], sulfonylation [31], and sulfonylation [32] reactions of thiocarbonyl compounds appeared. Furthermore, the preparation and characterization of sulfuranes [33], a remarkable class of compounds with hypervalent sulfur, was described.

In the 1980s, Walter and his coworker Hühnerfuss started investigations on monomolecular surface films, which soon evolved to environmental research when these studies focused on films on sea surfaces [34]. H. Hühnerfuss and his group continued and extended these experiments which then developed into far-reaching international projects.

After his retirement in 1986 Walter devoted himself even more decidedly to the pursuit of historical questions than during his active time. The history of science had always fascinated him. He was a member of the section "Geschichte der Chemie" of the "Gesellschaft Deutscher Chemiker" (GDCh). He published fascinating articles for example on August Kekulé [35], on chemical symbols [36], on the Nobel Prize winner Otto Stern, who had been expelled from his professorship at the University of Hamburg by the National Socialists in 1933 [37], on the history of sugar [38], or on Paracelsus [39]. In addition, he wrote essays about historical topics concerning the University of Hamburg and its institutions [40, 41, 42, 43, 44].

Walter's reputation is not only documented by more than 250 articles in scientific journals but also rests on a renowned textbook ("Beyer-Walter") [45]. From 1971 on, he prepared 24 editions, which he always brought up-to-date. The "Beyer-Walter" was translated into English [46], and Walter was amused to learn that in 1989 an obviously pirated Chinese edition of the textbook had appeared. Furthermore, Walter was Associate Editor of the well known journal *Phosphorus, Sulfur, Silicon and the Related Elements*. He was one of the initiators and promoters of the *International Symposium on Organic Chemistry of Sulfur (ISOCS)* serving as chairman of ISOCS VII in Hamburg in 1976, as well as of the *European Symposium on Organic Chemistry (ESOC)*.

Beyond his engagement in the science of organic chemistry Walter's strong efforts were always directed to the University of Hamburg as a "republic of letters" in its entirety [40, 41, 42, 43, 44]. Firstly, he was decidedly involved in the creation of the new chemistry buildings (1960–1964). In 1964, he was appointed Professor für Theoretische Organische Chemie, which rather meant physical organic chemistry in Germany at the time. Since then he accepted responsibilities for a plethora of academic functions, which is evidence of his untiring power and zest for working and also of his abilities as administrator. He was Dean of the Department of Chemistry (1970–1972), member of the University Council and the Academic Senate for many years, and Director of the Institute of Organic Chemistry and Biochemistry (1975–1986). In addition, he was active as confidential professor of the Studienstiftung des Deutschen Volkes (German National Academic Foundation). In 1984, he was decorated with the Ehrenzeichen des Deutschen Roten Kreuzes (Honorary Medal of

the German Red Cross), for his 45 years of engagement as the protector of their students' hall of residence [47]. The Joachim-Jungius-Gesellschaft der Wissenschaften (now Academy of Sciences and Humanities in Hamburg) in 1993 awarded him the Joachim-Jungius medal in recognition of his merits as a member of many years' duration and his presidency of the society (1972–1975).

Despite his numerous official activities, Wolfgang Walter always remained a charming man and a philanthropist. He was a great host—well known for his connoisseurship and the corresponding wine tasting parties. His art of living, his high spirits, and his optimistic approach to everything set an example to all of us. He will be missed not only by his former students, but also by the world-wide sulfur community.

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