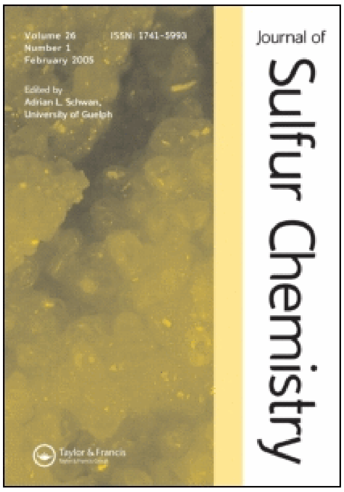

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Researches in organosulfur chemistry by a non-organosulfur chemist

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Researches in Organosulfur Chemistry by a Non-Organosulfur Chemist

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Henry Shine was born in England in 1923 into a working-class family. The field of chemistry as a potential career opened up for him with his appointment as a laboratory assistant, during the war, first at McLean's Pharmaceutical Company in 1940 and then at Pear's (a branch of Lever Brothers) soapworks in 1941. From Pear's and being a part-time, night-school student, he went in October 1942, with a war-time Government's blessing, to be a full-time university student at University College, London, then evacuated to the University College of Wales in Aberystwyth. He obtained a 1st Class Honours B.Sc. degree in 1944 from the bustling department of the Hughes-Ingold pairing. After a short stay with Shell Oil Company he took up research with Professor E. E. Turner on a war-time project at Bedford College, London. He received the Ph.D. degree in late 1947 and went immediately in January, 1948, to Iowa State College for a brief spell of postdoctoral work (with Henry Gilman) and independent research. He joined Carl Niemann at Caltech in the fall, 1949, for postdoctoral research in enzyme kinetics. He became a research chemist with the U.S. Rubber Company in Passaic, NJ in the fall, 1951, and left in the fall, 1954, to become assistant professor of chemistry at Texas Technological College (now Texas Tech University). He was chairman of Tech's Department of Chemistry during 1969–1975 and was designated Paul Whitfield Horn Professor of Chemistry in 1968. He was an Alexander von Humboldt distinguished senior scientist during 1986–1987. He is a member of the American Association for the Advancement of Science, American Chemical Society, Royal Society of Chemistry and Sigma Xi.

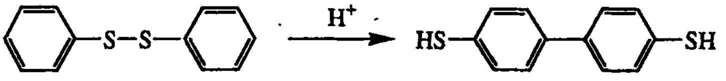
The following wonderfully personal chemical autobiography recounts how he became a sulfur chemist by accident, but then a leading organosulfur chemist. The account illustrates well how his keen insight and perseverance resulted in the seminal development of organosulfur cation radical chemistry.

At the end of the first paper in this series, the writer, C. S. Marvel, says "I have never considered myself a sulfur chemist".[1] When I read that declaration, after having been invited to write an article for the series myself, my immediate response was "me, too, Speed". Marvel, nevertheless, lists 99 publications in organosulfur chemistry! Furthermore, he describes how he began his research in polymerization of alkenes by sulfur dioxide as the result of a chance observation by a chemist at DuPont (presumably where Marvel was on a consulting trip). Like Marvel, my work in organosulfur chemistry, if I may call it that, began also by chance. Nothing in my early training had any connection with or could have guided me into sulfur chemistry. My contributions to this field came principally from studying the chemistry of the thianthrene cation radical, and that in itself developed quite accidentally. This story, then, is of how it all happened.

I grew up in England, where, during the years 1945–1947 I worked with Prof. E. E. Turner at Bedford College in London, on a wartime project, the synthesis of pure hydrocarbons. That project gave me a Ph.D. degree and a consuming interest in the mechanisms of Grignard reactions, whose anomalies were so striking in the syntheses we carried out. Consequently, in January, 1948, I journeyed to Iowa State College, in Ames, IA, to seek guidance from Prof. Henry Gilman in studying the enolisation, condensation and reduction reactions caused by Grignard reagents. These studies were not really fruitful, and on being viewed 45 years later, from the vantage point of esr and electron-transfer reactions, my interpretations of the reactions now look naive, if not foolish.[2] At Iowa State, however, events which don't need describing here led to an abridgment of my association with Gilman and my working independently. At the same time I became an instructor in a "quiz section" in undergraduate organic chemistry, during which an undergraduate's question about the mechanism of the benzidine rearrangement led further to my teaming up briefly with George Hammond during early 1949 and discovering that the acid-catalyzed benzidine rearrangement was second order in acid. None of this would appear to have any connection with sulfur chemistry, but as you will see, the benzidine rearrangement was, in fact, responsible for my becoming, even if under false colors, a sulfur chemist. I will say very little more about the benzidine rearrangement, because my assignment here is to account for my being a sulfur chemist. The story of my early foray into the benzidine rearrangement, and how it affected my research life, has been described elsewhere.[3] Here, I will describe how those few months in 1949 caused me later to spend much of my research life in organosulfur cation radical chemistry.

Were you to read my resumé, you would find that I left Iowa State in 1949, spent two years at Caltech (with Carl Niemann), and three years with the U.S. Rubber Company in Passaic, N. J. (U.S. Rubber is now Uniroyal, and is in Middlebury, Conn.) In the Fall, 1954, I left U.S. Rubber and became an assistant professor of chemistry at the little-known Texas Technological College (now Texas Tech University).

As with most beginners in academic life, my first choices of topics for research were from earlier experiences. I and my students began studying acetyl peroxide chemistry (a development from U.S. Rubber days) as well as benzidine rearrangements, but thermal ones. In connection with the benzidine rearrangements, though, I believed that there should be a sulfur analogue of the rearrangement of hydrazobenzene. It was a trivial idea, but I wanted to find out if it would occur. The product, from diphenyl disulfide, would by analogy be biphenyl-4,4'-dithiol (eq. 1). In 1956, therefore, I asked one of my early graduate students, John Bear, to study this reaction, and because of the anticipated low basicity of diphenyl disulfide, I suggested that he use concentrated sulfuric acid. John's notebook shows that he began the work on November 17, 1956.



(1)

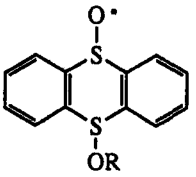
It is fortunate, in retrospect, that at that time I knew nothing about the chemistry that was to develop. I had not gone to the literature, where I would have found that the reactions of diphenyl disulfide with conc. H_2SO_4 had been reported years earlier in Germany, in 1909, by Fries and Volk,[4] and were also being studied in the USA by Szmant[5] at the time I began. I knew nothing about the thianthrene that was to make itself known and had never heard about esr spectroscopy. This knowledge was to evolve from Bear's beginnings, but had I read the literature first I would probably have been put off by the seeming complexity of the work and would not have begun. At that time (1956), also, I was more interested in benzidine rearrangements and in reactions of diacetyl peroxide with alkenes such as cyclohexene. So, the diphenyl disulfide work was a sort of peripheral affair, and had I read up on diphenyl disulfide in the old literature, it is probable that I'd have found something else for John Bear to do.

At any rate, the reaction of diphenyl disulfide with conc. H_2SO_4 turned out to be messy. When diphenyl disulfide first dissolves in conc. H_2SO_4 the solution becomes green and later purple. By pouring the solution onto ice, Bear was able to isolate a small amount of a crystalline substance that turned out to be thianthrene, but the bulk of the product was, we believed, a polymer, formed, we proposed, from the rearrangement product, biphenyl-4,4'-dithiol (**2**), the very product we had anticipated (eq. 1).[6] What I hadn't anticipated in 1956 was that if **2** did form, it might polymerise by oxidation. Bear found in August 1957 that a solution of thianthrene in conc. H_2SO_4 was purple, hence accounting for the purple color of his aging solutions of diphenyl disulfide. We had not traced Stenhouse's early papers that reported the same finding with thianthrene 100 years earlier![7] As the literature was to show, though, all of Bear's work had already been tried many years earlier. He also made the dithiol (**2**) and studied its reactions. He worked with di-*p*-tolyl disulfide, too, but becoming discouraged with the work left it for a nice career in inorganic chemistry. I, myself, eventually tackled the meaning of the purple solutions.

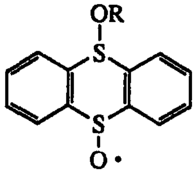
My notebooks show that I took on the thianthrene problem in 1959. By that time I had learned about the early German work on reactions of thianthrene (Th) in conc. H_2SO_4, and of its 5-oxide (ThO) in that acid and in others, such as HCl. I had also learned something about esr spectroscopy and that the literature showed that the purple solutions of Th and ThO in conc. H_2SO_4 each had a 5-line esr spectrum. The esr spectroscopy was reported by physicists like Fraenkel at Columbia (1953)[8] and Wertz at Minnesota (1955),[9] because physicists at that time were building their own esr spectrometers and beginning to interpret the spectra they gave. No one in the early 1950s knew what caused the 5-line esr spectrum, however.

In 1957 a publication appeared by Fava, Sogo and Calvin at Berkeley.[10] They worked with Th but most of their work was carried out with solutions in trifluoroacetic acid. These workers deduced that the purple color of the solutions in H_2SO_4 was caused by the tautomeric free radicals **3** and **4**, and by the corresponding trifluoroacetate radicals (**5** and **6**) in CF_3CO_2H. It was obvious to me that this couldn't be right because these radicals, even if they were tautomeric, could not show a 5-line esr spectrum attributable to four equivalent protons. Their esr spectra should have been from two inequivalent sets of two protons. Calvin's group believed that these radicals were formed in a disproportionation reaction between ThO and the 5,10-dioxide (ThO_2), each being formed from Th somehow in solution.

When I began my work, then, I was not so much interested in thianthrene only but also in the reactions of ThO and the 5,10-dioxide, ThO_2. I spent a lot of time studying with absorption spectroscopy the conversion of ThO in conc. H_2SO_4 into the same purple solution that was obtained with Th in conc. H_2SO_4.



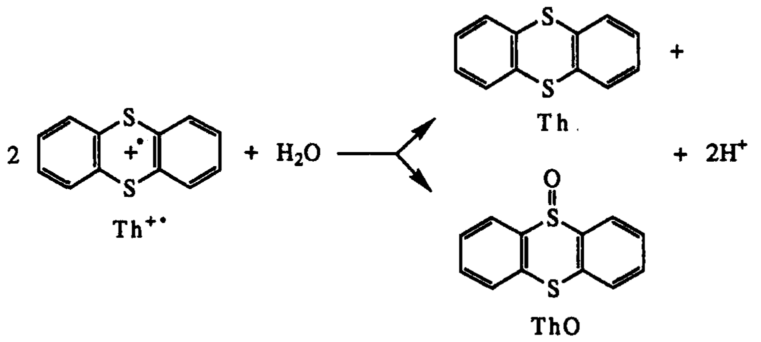
3, R = H
5, R = $-COCF_3$



4, R = H
6, R = $-COCF_3$

The Robert A. Welch Foundation, by that time, was supporting my work and had bought me a Beckman DK-2 recording spectrophotometer (now junked) with which I spent month after month doing spectroscopy in conc. and fuming H_2SO_4. Eventually, in 1960, I deduced from these studies, but did not feel ready to publish, that the purple color had to be caused by something that was entirely new to me, a cation radical, now the well-known $Th^{\cdot +}$. It is odd to realize that Fava, Sogo and Calvin had this structure in their 1957 paper but looked upon it as an intermediate in arriving at the radicals **3–6**.

My old notebooks show how surprised I was at finding that, when purple solutions of Th in conc. H_2SO_4 were poured onto ice, both Th and ThO were formed and in equal amounts. More surprising was the finding that purple solutions of ThO in conc. H_2SO_4 gave these products too. Eventually, I deduced that the reaction taking place was the now famous one (eq. 2). This was the



(2)

first real cation-radical reaction to be studied. Eventually, again, its mechanism was to form the basis of many other studies.

A new development in my education came in October, 1960. Varian Associates held one of its free training sessions for people who wanted to learn about esr and nmr spectroscopy. I was fortunate in being selected from among the many applicants. It was at this workshop that I met Glen Russell and Michael Szwarc and they have remained friends since that time. Michael Szwarc, from Syracuse School of Forestry, became the founder of Gordon Conferences in Radical Ions, and chaired the first Conference in 1968. Glen Russell chaired the second in 1970, and I followed with the fourth, in 1974.

The workshop in Palo Alto in 1960 was thrilling. I worked with a young man named Larry Piette, not knowing until I read of his death that he was 10 years my junior. Larry Piette died on November 17, 1992. He was, or had been until he became so ill, Dean of Graduate Studies at Utah State University in Ogden.

But, in that week in October, 1960, Larry Piette characterized my conc. H_2SO_4 solutions with the soon-to-be-famous 5-line esr signal. More important, he fitted up one of the newly-designed Varian electrochemical esr cells, to show that the species causing the 5-line spectrum was obtainable by anodic oxidation of Th in nitromethane solution. How well I remember that day. Larry set up the experiment and switched on the anodic current. To my great disappointment no sign of an esr signal appeared. Undaunted, Larry said "let's go to lunch and leave the current on". His esr machine was also newly designed to allow for the repetitive cycling of magnetic field. So we went to lunch and when we came back to the lab, to my great joy, there was a most beautiful sight on the length of strip-chart paper hanging from the small G-10 recorder—a magnificent 5-line esr spectrum.

I returned to Lubbock with two prizes: the anodic esr spectrum and Larry Piette's agreement to collaborate on quantifying my sulfuric acid solutions and their esr spectra. During the following months I sent Larry Piette, through the U.S. mail, a series of solutions of Th and of ThO sealed in not only conc. H_2SO_4 but also fuming H_2SO_4. His job was to relate esr signal intensity to my solutions whose concentrations I kept secret from him. In the meantime, in Lubbock I kept up with the absorption spectroscopy and also with the quantifying of products. I was in no hurry to publish our work, but that was because I was still rather naive; there was no concept of tenure at Texas Tech and the current publish-or-perish way of life was unknown. By the time the work was published in 1962,[11] two other researchers had made the same deduction about the structure of $Th^{\cdot +}$. They were Kinoshita[12] in Japan and Lucken[13] in Switzerland. They, too, published in 1962, and not one of us knew of the others' interests prior to publication. None of us knew, also, of the Ph.D. work of W. C. Needler at the University of Minnesota.[14]

At about this time, with grant money from the Air Force Office of Scientific Research, I was able to buy a Varian 4502 esr machine with its, then, small, six-inch magnet. I went to the famous Bell Labs in New Jersey to learn how to use it and how to calibrate esr spectra. The wonderfully hospitable Bell people gave me a list of their equipment and a diagram on how to set it up. I bought it all: frequency counters, fluxmeter, and all the electronic bits and pieces, and set them up with the 4502 in a room next to my office. Bell's esr spectroscopist, Bill Yager, was very kind and patient with this idiot-child from Texas. With the

4502, students Charles Dais and Bob Small recorded the esr spectra of numbers of substituted thianthrene cation radicals, allowing us to deduce the origin of the 5-line esr spectrum—the strong coupling with the four protons in the 2, 3, 7 and 8 positions.[15] Some years later, Paul Sullivan (a much more skillful esr spectroscopist than I) collaborated with me in getting the whole of the resolved esr spectrum: 25 lines for the protons and 4 lines for naturally abundant ^{33}S.[16]

With the 4502 we went from thianthrene to phenoxathiin, phenothiazine, dibenzodioxin, and selenanthrene and were able to explain much of the chemistry that had been reported so well in German literature in the 1910s to 1930s.

During the period 1960–1968 most of our efforts in Lubbock were in characterizing spectroscopically the oxidized forms of the sulfur heterocycles. In one effort, designed to link spectra with species, one of my students, Dan Thompson, showed with freezing point measurements that the thianthrene dication was formed from thianthrene 5-oxide in 100% sulfuric acid.[17] I had recalled that one of my classmates from the 1942–1944 days in England, Ronald Gillespie, had perfected making such sulfuric acid measurements in his research with C. K. Ingold on the nitronium ion, so in Lubbock, we decided to build the same system with vertically moving, magnetized stirrer that Gillespie described.[18] There being no glassblower and suitable shop facilities at Texas Tech then, however, I arranged to have the apparatus built by Ace Glass in New Jersey. It worked splendidly. We still have the equipment, a museum piece now. My publications of that period contain drawings of ultraviolet and visible spectra of cation radicals and dications recorded over times of reaction and showing beautiful isosbestic points as one species changed into another. The drawings submitted in these early publications were glossy prints made with the help of the local portrait studio, Reeve's Photographers. The photographers there, Winston Reeves and Harold Roddy, taught me how to paint out, with photographer's rouge and tape, the blemishes in the negatives they had made of my DK-2 charts. They supplied me with the blades and brushes and paint, tools I still have, more museum pieces. That was a very pleasing period, during which I came also to admire so much the early work of pioneers (Fries, Pummerer, Kehrmann, for example) in that area of chemistry, who recorded absorption spectra under such very different, difficult conditions and had a very sound feeling for the oxidation states being encountered. The clues to interpreting the esr spectra of the 1950s were buried and unseen, it seems, in some of these early works, particularly those of Kehrmann who, with phenothiazine and its derivatives, identified what he called the semiquinoid (cation radical) and holoquinoid (dication) states. I have described this period in some detail earlier.[19] I became so impressed with Kehrmann's work that I tried to trace all of his writings via the name index of Chemical Abstracts. Alas, the last entry I came upon was to his obituary. He died on March 4, 1929.[20]

In the late 1960s the work at Texas Tech began to turn from spectroscopic characterizations toward reactions of the sulfur heterocycle cation radicals. The first to be tackled mechanistically was of $Th^{\cdot +}$ with water. Our proposal, that reaction was with the dication (Th^{2+}), formed by disproportionation of $Th^{\cdot +}$,[21] was shown to be wrong by Parker and Eberson, reaction occurring, in fact, with $Th^{\cdot +}$ itself. This reaction became a sort of cause celebre in cation radical chemistry. Its complexity, as to the order in water, particularly, has been described by Hammerich and Parker[22] and also by Vieil.[23] From reaction with water we went on to reactions of thianthrene, and phenoxathiin cation radicals with ammonia and primary and secondary amines. These reactions led to sulfilimines and dialkylaminosulfonium salts. It was during these studies that Nita Silber[24] discovered that thianthrene cation radical perchlorate exploded if not treated properly. When being scraped from a fritted glass filter funnel, the solid salt blew up, fortunately without doing her permanent hurt. Reactions with ketones, organomercurials, alkenes and alkynes followed. The reactions with organomercurials turned out to be propitious. The reactions appeared to lead to the formation (and trapping by $Th^{\cdot +}$) of radicals ($R\cdot$) from a fleetingly formed dialkylmercurial cation radical ($R_2Hg^{\cdot +}$).[25] This led us to attempt to generate alkyl radicals by photolysis of an azoalkane in a solution of $Th^{\cdot +}$. We found, thereby, that the azoalkane we had chosen (azoisobutane) was itself rapidly oxidized by $Th^{\cdot +}$ to the *tert*-butyl cation. Out of that finding came a long series of studies of reactions of $Th^{\cdot +}$ with azoalkanes and a 10-year collaboration in that chemistry with Prof. Paul S. Engel, an expert in azoalkane chemistry, of Rice University. The results of that collaboration can be seen in the list of my organosulfur publications. Fortuitous use of a primary azoalkane (which tautomerized unanticipatedly into the hydrazone) by Mr. (now Dr.) Mansurul Hoque led to our discovery of the oxidative cyclization of aldehyde hydrazones into 1,2,4-triazoles.[26] In turn, this work led to our studying the cyclizations and cycloadditions, caused by reaction with $Th^{\cdot +}$, and other cation radicals with greater oxidation potential, of the arylhydrazones of aromatic aldehydes and chalcones, of oximes and semicarbazones. Thus, we entered into areas of heterocyclic chemistry quite by accident. The work continues, too, with Mr. Hari Das Mandal.

Similarly, the early work with dialkylmercurials that was initiated by Dr. B. K. Bandlish in the 1970s,[27] led to a series of investigations of electron transfer reactions of organometals (mercurials, Grignard reagents and organotins) that spanned 10 years and still continues (with Mr. Sang Rok Do).

At the time of writing this historical and personal summary, work with $Th^{\cdot +}$ continues and harks back to the first of our studies, that with water. It seems obvious that if water reacts with $Th^{\cdot +}$, alcohols should, too. Attempts at such reactions were, in fact, made 20 years ago by Mr. Kyongtae Kim,[28] but were too difficult to sort out for the lack of GC equipment. Now however, Mr. Wang Yueh has worked with $Th^{\cdot +}$ and a large number of alcohols and diols and has characterized the reactions quantitatively. Oxygen-atom transfer occurs with the formation of ThO and products of concordantly formed alkyl cations. A simplified reaction stoichiometry is given in eq. 3, analogous entirely to that of the

$$2\,Th^{\cdot +} + ROH \longrightarrow Th + ThO + R^{+} + H^{+} \qquad (3)$$

water reaction. In the reaction with an alcohol the amount of ThO formed is equal to the sum of the amounts of products from R^+. Equation (3) is simplistic in that in some reactions products are formed, it appears, without originating explicitly from a carbonium ion. A preliminary report about cyclohexanols has been made.[29]

There is yet one part of the thianthrene chemistry which remains unsolved and still puzzles me. It is, in fact one of the very earliest of reactions to have been reported, the conversion of ThO (thianthrene 5-oxide) into $Th^{\cdot +}$ in conc. H_2SO_4 (eq. 4). At one time Dr. Joseph Fong[30] and I tried to study the reaction

(4)

kinetically but could not get reproducible results. I have speculated that the oxygen atom of ThO is transferred to the ring of another ThO molecule,[18] and have used in support of that speculation the isolation of hydroxylated ThO much earlier by another coworker, Dr. Thomas Robinson.[31] This conversion of ThO into $Th^{\cdot +}$ is probably related to the reductive chlorination that ThO undergoes in conc. HCl solutions. I tried to study that myself, too, but failed to get anywhere with it. It is unlikely that I will return to these reactions, but my curiosity about their mechanisms is undiminished.

This short and rather personal story of my becoming a sulfur chemist is one of chance, of a research life initiated by an undergraduate's question 45 years ago in Iowa. Most, if not all, of my readers can tell a similar story if only amounting to the fateful choice of research advisors in graduate school days. Had I responded more favorably to a solicitation by E. D. Hughes in my undergraduate days in England, I may have begun research in the distinguished school of Hughes and Ingold instead of going my own way in industry (Shell Development Company, in 1944) and joining Prof. E. E. Turner later at Bedford College for Women. In that case my research and even personal life must have been quite different, and it is almost certain that I would not have wandered into organosulfur chemistry. I could not, however, have asked for more fulfilling experiences in research. Beginning with the invitation by Matthijs Janssen to speak at the Second Symposium on Organosulfur Chemistry in Groningen in 1966, at which I showed examples of isosbestic-point-laden absorption spectra in their untouched-up originality, I have attended organosulfur and related meetings all over the world and from them have made lasting friendships. For many years, this research has been carried out by clever students and postdoctoral fellows from widely scattered parts of the world. Some of these coworkers have settled in the United States, while others have returned to productive careers in their own countries, such as Argentina, India, Italy, Korea, Japan, and Poland. Their names appear in our publications, which I hope will stand the test of time.

ACKNOWLEDGMENTS

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Sciences, and the Robert A. Welch Foundation. Without this support the research would not have been possible. For it, I record here my indebtedness and thanks.

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PUBLICATIONS ON ORGANOSULFUR COMPOUNDS, PRINCIPALLY ON ORGANOSULFUR CATION RADICALS

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