

THE HISTORY OF OZONE. VII. THE MYTHICAL SPAWN OF OZONE: ANTOZONE, OXOZONE, AND OZOHYDROGEN (1)

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Introduction

It is a truth generally acknowledged that, a single chemist in possession of a good laboratory must be in want of a theory (2). Thus C. F. Schönbein (Fig. 1), the discoverer of ozone, wrote in an 1857 letter entitled "On the Various Conditions of Oxygen" which was read before the Philosophical Society in 1858 by his friend, Michael Faraday (3):

Be this, however, as it may, as we philosophers cannot do any notable work without having some hypothetical view in our heads. I shall place myself for some time under the guidance of the conjecture alluded to, and see what can be made out of it. If it leads to the discovery of some interesting facts I shall not feel ashamed of it, though it may turn out to be fallacious. We are but short-sighted men, and must be content with finding out a little bit of truth in wading through a sea of errors.

The modesty of the last sentence proved to be well justified.

Noyes and Kassel pointed out the danger involved (4):



Figure 1. Christian Friedrich Schönbein, Basel, 1799-1868 from Bull Hist Arch. Orig. photo from Univ of Basel Library

...the human mind is so constituted that it must have a picture as a working basis. Far too frequently, however, authors have been lead to form pictures and then to seek an interpretation of all data obtained subsequently in terms of these pictures, thereby overlooking many important points. It must be borne in mind that several different pictures will usually interpret a given set of data with equal exactness.

Schönbein's original proposal of ozone (5) had been based simply on odor. It had been a great success, winning from Berzelius (6) the comment that it was one of the most important discoveries in chemistry. Perhaps the ephemeral basis of its discovery prompted, in Schönbein and others, the notion that additional world shaking discoveries could be made on the

basis of minimal evidence. In the case of ozone, however, it should be pointed out that, within a year after its initial proposal, a large number of its properties had been established, unlike the substances described herein, which consistently eluded their pursuers.

This paper describes three examples from ozone chemistry of substances—antozone, oxozone, and

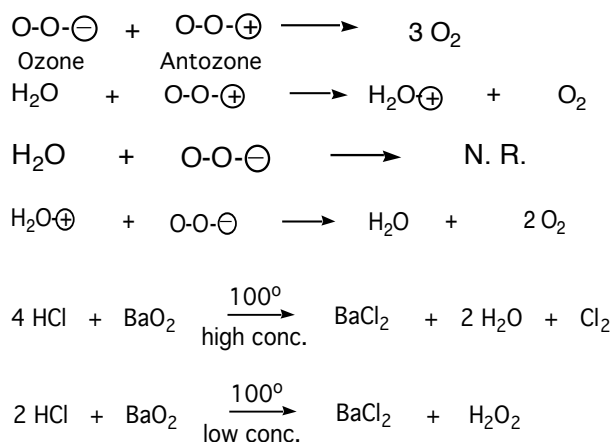
ozohydrogen—which were proposed by eminent chemists of their time in order to explain certain experimental phenomena. They consumed considerable research effort before disappearing from the literature.

Antozone

Schönbein was one of the outstanding chemists of the 19th century. In addition to the discovery and study of ozone, he developed commercial nitroglycerin explosives and studied a variety of physiological processes. He was particularly interested in an understanding of oxidation in chemical and biological systems. In this connection he came to the conclusion that some activated form(s) of ordinary oxygen was required for oxidation to occur. In a sense he was anticipating the idea of activation energy in chemical reactions. This consideration and the fact that ozone was formed by electrolysis led him to the idea that there were two species involved, negatively charged ozone $\text{O}-\text{O}-\ominus$ and a positively charged counterpart, antozone $\text{O}-\text{O}-\oplus$. Furthermore, the low yield of ozone obtained in electrolysis could be rationalized by assuming that two simultaneously formed but oppositely charged species neutralized one another to give ordinary oxygen; it was never clear why a small amount of ozone survived.

These ideas were first presented by Schönbein in an 1857 lecture before the Bavarian Academy of Science published in three parts in 1859 (7) and in the 1858 paper cited in the Introduction. The name antozone first appeared in a second 1858 paper (8). A succession of publications involving antozone appeared during the next five years (9).

Scheme 1



The great difficulty with antozone was that it was never possible to obtain a defined gas that could be recognized as a new substance with specific properties of its own, as had been the case with ozone 20 years earlier. There was no positive evidence for the existence of antozone. The best that Schönbein could do was to claim that antozone reacted with water to form hydrogen peroxide while ozone did not, so that the formation of H_2O_2 became a major criterion for the prior presence of antozone. Ozone on the other hand, did not react with water to form the peroxide but destroyed hydrogen peroxide, as shown in Scheme 1. This was explained by assuming an atom of antozone in H_2O_2 ; this reacted with ozone to give oxygen. He even developed (10) an improved analytical procedure for H_2O_2 . Another criterion was the reaction of metal peroxides containing antozone with HCl to liberate Cl_2 ; peroxides containing ozone did not undergo this reaction. According to this view, barium peroxide contained antozone ($\text{BaO}-\oplus$), lead dioxide did not ($\text{PbO}\ominus$). The weakness of this approach was the fact that it was only as valid as the choice of reaction conditions (see Scheme 1). Schönbein devoted much work to categorizing various substances as ozonides (containing negative oxygen) and antozonides (containing positive oxygen).

Thus Schönbein, an avowed doubter of the existence of atoms, was led to consider molecules in which one of the atoms bore a charge. This was actually not a new idea. Brodie (11) had proposed alternating charge polarization to explain certain kinds of reactivity ten years earlier; Schönbein, to Brodie's annoyance, did not cite this earlier work. In 1862 Brodie published a paper (12) in which, without ever mentioning the word antozone, he showed that reactions of metal peroxides could vary depending on the reaction conditions (Scheme 1). Among a number of examples was the reaction of barium peroxide with hydrochloric acid, which was shown to depend on HCl concentration: in dilute solution H_2O_2 was formed, in concentrated solution Cl_2 . Similar behavior was found for lead dioxide. According to Schönbein's criteria, the barium peroxide results indicated that this peroxide contains antozone when allowed to react with concentrated HCl but not with dilute HCl. Brodie wrote (12):

It is thus seen that those differences in the behavior of the different classes of peroxides, from which an imaginary distinction has been drawn between the oxygen respectively contained in them as positive or negative, are not fundamental and characteristic differences...nor are the peculiarities in the reactions of the oxygen of the alkaline peroxides of such a nature as to need any special hypothesis to account for them.

So much for antozone. Nothing further was heard from Schönbein on the subject of antozone, and he never referred in print to Brodie's paper.

An amusing side issue which has perpetuated the name of antozone came from geology. A fluorite mineral (German, *Flussspath*) studied in 1859 by the geologist (and musicologist) Schafhaeutl (13) in Germany gave off a bad odor and formed H_2O_2 when crushed. Schönbein obtained samples and leaped to the conclusion, because of the H_2O_2 formation, that the odor was due to antozone. The difficulties involved in the study of antozone are illustrated by Schrötter's attempt (14) to establish that the volatile substance was ozone. Schrötter passed the volatiles over a heated surface which would destroy ozone and then into KI solution. Unheated volatiles gave a strong positive test for iodine, whereas heated volatiles did not. He concluded the material was ozone, which was known to be thermally unstable (5). However, since the behavior of antozone on heating was not known, the result is consistent with ozone but not conclusive. After a long series of investigations, Becquerel and Moissan (15) showed in 1890 that free fluorine was present in such minerals and that the reaction of fluorine with water to form ozone (16) was responsible for the odor. Schönbein thought he had antozone in hand. In fact, his sense of smell had let him down. There is a family of fluorite minerals found all over the world that exhibit this behavior when crushed with water. They have been named antozonites and are the only survivors of the antozone theory.

The chemical community in general ignored antozone and wisely so. The major supporter of antozone after Schönbein was the physiologist, G. Meissner (Fig. 2), who had made important discoveries in physiology at an early stage of his career. Certain sensors in the body bear his name, and he advanced rapidly at an early age. Meissner spent the years 1855-1857 (age 26-28) as professor in Basel, where he apparently came under Schönbein's influence, although there is no evidence for any collaboration between the two, nor does Schönbein

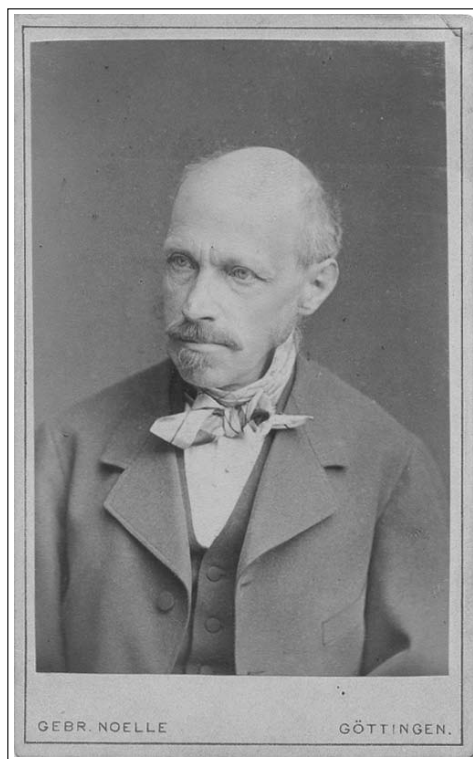


Figure 2. Georg C. F. Meissner, Göttingen, 1829-1905

refer to Meissner in any of his publications. After his move from Freiburg back to Göttingen in 1860 Meissner strayed in part far from physiology by carrying out intensive investigations on antozone even after Schönbein abandoned it. Instead of publishing in the journals of the time, his papers appeared in three bound volumes (17). Meissner observed that when ozone was passed into a solution of potassium iodide, which destroyed the ozone, a white fog was formed which passed through water wash bottles. He called this fog "atmizone" and later decided that it was identical to Schönbein's antozone. Upon standing for about an hour, the fog disappeared and droplets were formed in the vessel. Unfortunately, their composition was not studied in detail until the work of Engler and Nasse (see below). Meissner's analytical method for

establishing the presence of antozone was the appearance of this fog. Rothmund (18) investigated fog formation in some detail about 50 years later and showed that it was a general phenomenon in ozone systems and had nothing to do with antozone. Meissner's work was received in America with considerable interest, in the form of summaries by two distinguished American chemists (19).

The possibility that the fog contained hydrogen peroxide was ruled out since it passed through water. Both Babo (20) and Weltzien (21) suggested that it was nonetheless H_2O_2 . The matter was settled by Engler and Nasse in 1870 (22) who identified the fog unequivocally as dilute aqueous H_2O_2 by condensing it in cold traps followed by characteristic tests for H_2O_2 . They also showed that similar fog could be obtained by applying reduced pressure to aqueous H_2O_2 . So much for atmizone and antozone. Meissner continued his other academic activities but retired from research, apparently because of flawed results in some of his physiology research; but this may also have been related to the antozone fiasco. In Fox's 1873 book on ozone and antozone (23), one of the chapter headings is "Does the atmosphere contain antozone, alias the peroxide of hydrogen?" Leeds, summarizing the history of antozone in a very critical 1879 article, wrote (24):

By far the most important fact in the long and perplexing history of Antozone, is the recent discovery that there is no Antozone

All that remains is the designation of certain minerals and a valiant, if misguided, attempt to understand oxidation.

Oxozone

C. D. Harries (Fig. 3) was responsible for introducing the use of ozone into organic chemistry during the first two decades of the 20th century (25). In four summary articles of his ozone work (26, 27, 28, 29), as well as a collected volume of his ozone publications (30), he established the utility of ozone in organic synthesis and in structure determination of organic compounds. Harries established that the reaction of ozone with the double bond of an alkene gave a labile addition product ($R + O_3 \rightarrow RO_3$), to which he assigned the trioxolane structure **1** (Scheme 2) and gave the name ozonide (31).

Harries' procedure was to pass ozonized oxygen into cooled solutions of alkene in a volatile solvent (27) and then remove the solvent. In some cases the residue could be purified by distillation or crystallization (explosion hazard) and the product submitted to combustion analysis and cryoscopic molecular weight determination. In many cases, the addition of ozone to the double bond to form the ozonide was established by molecular formula; other methods for structure determination were not available; in fact, his trioxolane structure for the ozonide is not correct. If purification was not feasible, the crude reaction product was evacuated exhaustively and tested directly or separated into fractions on the basis of solubility or boiling point. Subsequent reaction of the ozonides, with water in the earlier years and later with zinc, afforded the familiar cleavage products, aldehydes and/or ketones and/or carboxylic acids.

However, at a fairly early stage in his investigations, products having the formulae RO_4 were also obtained (26, p 319; 27, p 289). This was observed to be a general phenomenon with carbonyl containing compounds and

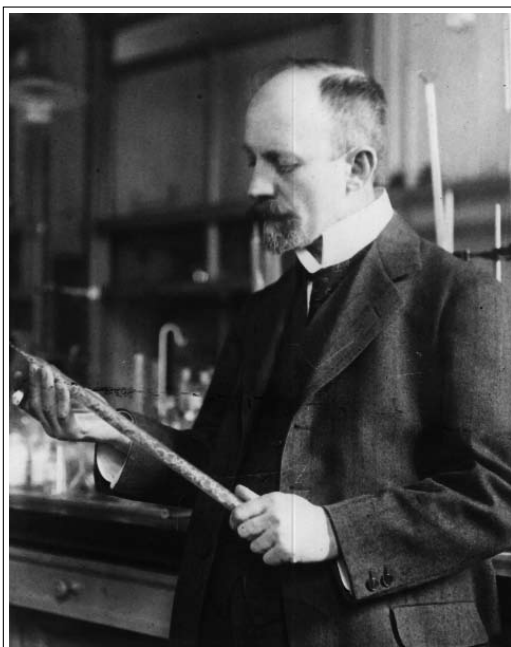


Figure 3. Carl Dietrich Harries, Kiel, 1866-1923
Photo from Siemens Archives

was attributed to the formation of peroxides which reverted back to the original carbonyl compounds on work-up with water. No such simple explanation was available for a number of alkenes possessing only the multiple bond but which formed, in addition to normal ozonides, products in which four oxygen atoms were incorporated (27). These included 2-butene, amylene, cyclohexene, pinene, and others (28).

Harries proposed that the products containing four oxygen atoms were formed from a new allotrope of oxygen, with molecular formula O_4 , which he named oxozone; its reaction with alkenes produced the addition products, oxozonides

($R + O_4 \rightarrow RO_4$). Interestingly, the output of Harries' ozone generator increased from about 5% ozone in oxygen in 1905 to as high as 14% by 1910 and close to 20% during the last years of his ozone work at Kiel, values much higher than reported by other laboratories where the silent discharge apparatus was used. These higher concentrations resulted in higher yields of oxozonides, suggesting to Harries that the production of oxozone was greater in these years. Further, base treatment of the initially formed gas mixture produced an effluent gas with reduced oxidizing power (reaction with KI solution) and produced only the "normal" ozonides. His conclusion was that oxozone is destroyed by alkali. The amount of oxozone in the original gas mixture corresponded to the reduction in oxidizing power on treatment with alkali and was on the order of one third or higher in a number of cases involving high ozone concentrations. Substances corresponding to dimeric ozonides (R_2O_6) and dimeric oxozonides (R_2O_8) were also obtained in some reactions, Harries suggested—but with no supporting evidence—that both O_3 and O_4 were in equilibrium with their dimers O_6 and O_8 and that the dimeric species were favored at lower temperatures.

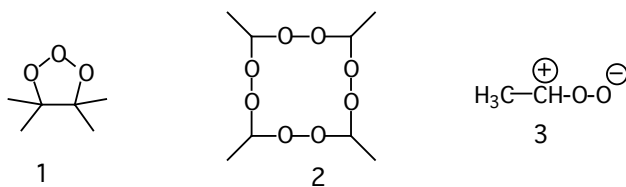
One might have thought that the proposed discovery of new allotropes of oxygen would have occasioned much interest in the chemical world. This was not the case, and rightly so as it turned out. Except for an occasional reference to an ozonolysis-induced product with an extra

oxygen atom, there seemed to be little or no interest in ozonone. As with antozone, there was no direct evidence for the existence of O_4 , nor are there any published reports of attempts to isolate it or obtain it in enriched form. In fact, within a short time (1922), Riesenfeld and Schwab (32) isolated pure ozone and reported that there was no evidence at all for a higher molecular weight component such as O_4 . Lainé (33), searching for an O_4 species in his studies of the magnetic susceptibility of ozone, also concluded that the product of silent discharge on oxygen was the single substance, O_3 . Except for one 1967 paper (34), it has not been mentioned in the literature for decades.

Less than ten years after Harries abandoned Kiel for Siemens and Halske, O_4 reappeared in a new guise. In 1924 Lewis (35) proposed it as a metastable dimer of molecular oxygen in order to explain the concentration dependence of the magnetic susceptibility of oxygen. Since then O_4 has flourished (36 and references therein) as well as higher allotropes (O_6 , O_8) of oxygen, none of them having any connection with the oxidative cleavage of alkenes.

Nonetheless, one must seek an explanation for why Harries went wrong. This was provided in 1942, 30 years after Harries' work, in an extensive paper on ozonolysis by Rieche, Meister, and Sauthoff (37). They repeated his ozonolysis of 2-butene and, following his manipulations, obtained a material with properties very similar to those described earlier and with a molecular formula $C_8H_{16}O_8$. This is the correct formula for the dioxozonide of 2-butene ($2 C_4H_8 + 2 O_4$) as proposed by Harries. However, Rieche identified it as the cyclic peroxide 2, (Scheme 2), the tetramer of the Criegee zwitterion 3 (carbonyl oxide) which is an intermediate in the ozonolytic cleavage of double bonds. The empirical formulae of the zwitterion, its oligomers, the addition product of putative O_4 to butene, and the dioxozonide are all identical – $(CH_2O)_n$!

Scheme 2



Harries' problem was his fertile imagination and the limited knowledge he had available to him on the structures of the intermediates in ozonolysis. Aside from empirical or molecular formula, he had no other evidence;

nor had work progressed to an understanding of the detailed mechanism of alkene–ozone chemistry. Part of the problem was his use of acetic acid in the determination of molecular weights, which leads to decomposition reactions; Rieche et al. used benzene as solvent in their cryoscopic measurements.

A second explanation was the possible occurrence of additional reactions of ozone, particularly with the high ozone concentrations of the later Kiel years. The reaction of ozone with C-H bonds to produce alcohols is well documented, albeit slower than the reaction with double bonds; its rate would be enhanced by the high ozone concentrations. This was briefly considered by Harries and discarded because he claimed, interestingly, to have interrupted the reactions as soon as the alkene was consumed.

Ozohydrogen

In 1853 Osann (G. not H.) (Fig. 4) reported that acid solutions of metal salts, particularly silver salts, deposited the metal at the cathode upon electrolysis (38). He went on to record this same observation in a number of additional papers (39). A further observation was that these reductions were not achieved by chemically generated hydrogen gas but only upon electrolysis. Based on the analogy that oxygen is converted in part to ozone upon electrolysis, Osann proposed from the beginning of his work that the reductions were effected by a new, active form of hydrogen which he called ozohydrogen. The name implied it had the molecular formula H_3 ; another name was hyzon. Considerations of bonding did not come into play in 1853. Ozohydrogen could, according to Osann, be stored for long periods of time without losing its special reducing power (39). Osann's papers were summarized uncritically by Jensen (40) in 1990 in a very interesting article on the nascent state.

Apparently Osann was completely unaware of the fact that Hisinger and Berzelius (41), 49 years before his work, had proposed that electrochemical reactions could be effected by direct interaction between the electrode and species in the solution being electrolyzed, or indirectly by formation of an intermediate that reacted further. He also apparently had no knowledge that electrodeposition of metals was well-known; a patent had been granted in 1840 for electroplating with gold or silver, and commercial application had followed. The generally accepted point of view had been that the reaction was a direct one, involving the electrode and the metal in solution and thereby completely independent of any species of

hydrogen. It should be noted that Faraday, who initially supported this view (42) later favored an indirect reaction involving nascent hydrogen formed at the electrode. Five years after Osann's first report, Magnus (43) did address the question of the mechanism of the silver precipitation. He reported that a new American student, "Dr. Dean," had arrived in his laboratory and been given this as a research problem. When Dean failed to reproduce Osann's results on the activity of electrolytically generated hydrogen, Magnus himself made two attempts, and, luckily for Dean, also failed to reproduce Osann's results. Silver was only deposited during the time when current passed through the solution. Magnus came out unequivocally on the side of a direct electrochemical reaction, which is clearly, in modern perspective, correct. None of this had any influence on Osann, who continued to publish his work with ozohydrogen, his last paper on the subject appearing in 1864, two years before his death.



Figure 4. Gottfried Wilhelm Osann, Würzburg 1797- 1866.

This is a very curious story involving a complete neglect of the chemical literature; the only citations in all of these papers are a few references to Osann's own work, mainly to lectures he presented in Würzburg. Osann was not an amateur chemist as can be seen in the biographical section of Ref. 37; he was also rector of his university for some years.

H_3 , however, has been a subject of interest for many decades. It first reappeared about 50 years after Osann's work in Thomson's studies on cathode rays (44) with the detection of a species having $m/e = 3$, which he designated X_3 and considered most probably to be the cation of

triatomic hydrogen. Three years later Dempster obtained the same species in relatively high concentration (45).

A number of reports of H_3 appeared later in the literature but were shown by Smallwood and Urey to be due to insufficient attention to blank experiments (46 and references cited therein). Herzberg has provided an interesting account of his accidental discovery of the spectrum of H_3 (47). Triatomic hydrogen continues to be a subject of interest to the present day but bears no resemblance to Osann's reducing agent for metal ions in solution.

Sin in Chemistry

In the years preceding his retirement and immediately after (1985-1995), the author of this paper presented a lecture entitled, "Sin in Chemistry—Mistakes and Fraud in the Chemical Literature," at institutions in Europe, North America, Australia, and New Zealand. The essential point was that the chemical literature is the repository of our knowledge of chemistry, and we chemists have a moral commitment to publish material that is as close to the truth as we can possibly get. Fraud is, of course, the ultimate sin and should be punished with excommunication (for a prime example of fraud see Ref. 48). Mistakes cover a wide range, from trivial issues like typographical errors to premature publication before serious examination of results, or fundamental mistakes in interpretation. Among the lesser, but real, sins is the proposal of new substances without any real evidence for their existence. Speculation, even wild speculation, is entirely appropriate in private but should not take up space in the chemical literature until it has a reasonable degree of real support.

Sin is rampant in all three of the supposed substances discussed in this paper. Interesting new compounds were proposed without serious attempts to establish their existence. The result in all three cases was the expenditure of considerable useless effort, which encumbered the chemical literature without contributing anything of value.

Schönbein wrote in his first paper on antozone that (3):

If it (his conjecture) leads to the discovery of some interesting facts I shall not feel ashamed of it, though it may turn out to be fallacious.

It did not lead to any interesting facts, and he should have been ashamed of it. In his case, at least he was attacking a fundamental problem, the nature of combustion.

When Brodie demolished his scheme, he abandoned antozone.

His partner in sin, Meissner, is subject to more serious criticism. He considered antozone to be the fog formed with ozone under certain conditions. Upon standing, this fog condensed to leave droplets in its container. No attempt was reported by Meissner to determine the constitution of those droplets. Had this been done, as it was years later by Engler and Nasse, it would not have been difficult to establish that one was dealing with dilute aqueous hydrogen peroxide, and that would have been the end of it.

Harries' oxozone is another case where a substance was proposed without any real evidence for its existence, nor was any ever obtained. At least it can be said in his defense that his experimental procedures were sound. Rieche successfully repeated his work in order to obtain the tetramer **2** and establish its structure. If one skips over the oxozone and O_4 parts in Harries' papers, there is no problem. Unfortunately, there are many such discussions in his papers. He also proposed new allotropes of oxygen, O_6 and O_8 , which had no basis in fact.

Osann's ozohydrogen work can only be described as an aberration. He overlooked a considerable body of earlier work; some of his key results could not be reproduced, and he ignored criticism. Inquiries at the University of Würzburg established that he was rector of the university in the late 1840s (and apparently a progressive rector at that) but provided no insights that might have explained his behavior with ozohydrogen.

As already noted, all three of the imaginary substances discussed here disappeared quickly from the chemical literature after their initial proponents ceased to support them. The chemical community of their time showed very little interest, in contrast to the considerable activity in ozone chemistry as soon as ozone's existence was proposed by Schönbein. The common wisdom operated well.

Summary

Three substances, antozone, oxozone (O_4), and ozohydrogen (H_3), were invented, the first and third in the mid-19th and the second in the early 20th century, in order to explain certain experimental facts. None of these substances could be isolated or characterized, each serving as a rationale for certain experimental results and consuming considerable experimental effort while contributing a minimum to chemical knowledge.

Antozone was proposed by C. F. Schönbein to explain various observations in ozone chemistry and oxidation reactions in general. It was, at least, a valiant attempt at the understanding of oxidation reactions and can be said to be an early expression of the idea of activation energy in chemical reactions. Oxozone was proposed by Harries to account for the presence of one too many oxygen atoms in some products of ozonolysis of olefins but turned out to be the result of formation of ozonolysis products which were not known at the time of his work. Ozohydrogen, a special form of hydrogen with unique reducing power, was an invention of Osann which lacked any merit whatsoever. All three of these "substances" died with their inventors.

In his first paper on antozone, Schönbein wrote (3):

We philosophers cannot do any notable work without having some hypothetical view in our heads.

While this is a valid point of view, it is usually best to keep such hypothetical views unpublished until they can be supported.

ACKNOWLEDGMENT

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 13. K. F. E. Schaffhäutl, "Ueber den blauen Stinkfluss von Wölsendorf in der Oberpfalz," *J. Prakt. Chem.*, **1859**, 66, 129-136. Karl Franz Emil von Schaffhäutl, 1803-1890. Studied medicine and chemistry. From 1834-1841 in England involved in steel production. In 1842 Assoc. Prof. Geology and Paleontology Univ Munich, Prof. 1845. Member Bavarian Academy of Science. Also a musicologist.
 14. A. v. K. Schrötter, "Ueber das Vorkommen des Ozons im Mineralreiche," *Ann. Phys. Chem.*, **1860**, 192 (111), 561-572. Anton Schrötter (von Kristelli), 1802-1875. Studied with Liebig in Giessen. Prof. Chem. and Physics, Johanneum, Graz, 1830. Prof. Chem., Tech. Hochschule Wien, 1845-. Secretary Vienna Acad. 1850-. Discovered an amorphous form of phosphorus..
 15. H. Becquerel and H. Moissan, "Étude de la fluorine de Quincé," *C. R. Séances Acad. Sci., Ser. C*, **1890**, 111, 669-672 and references therein (a paper by two Nobel prizewinners). Antoine Henri Becquerel, 1852-1908, (son of the noted physicist Alexandre Edmond B. 1820-1891). Discovered radioactivity and shared 1903 Nobel Prize with Mme Curie. Henri Moissan, 1852-1907. Prof., École supérieure de pharmacie in Paris. Prof. of Chem. Univ of Paris. Nobel prize 1906 for his contributions to fluorine chemistry. .
 16. H. Moissan, "Production d'ozone par la décomposition de l'eau au moyen du fluor," *C. R. Séances Acad. Sci., Ser. C*, **1899**, 129, 570-573.
 17. G. C. F. Meissner *Neue Untersuchungen über den elektrisirten Sauerstoff*, Göttingen, bei Diederich, 1869; *Untersuchung über die elektr. Ozon erzeugung, etc.* Reprinted from *Abhandl. der K. Gesell. der Wissenschaften zu Göttingen*, Göttingen, 1871; *Untersuchungen ueber die elektrische Ozonerzeugung und ueber die Influenz-Elektrizität auf Nicht-Leiter*, Göttingen, 1871; Hahn: Hannover, 1869. Georg C. F. Meissner, 1829-1905. Studied in Munich, Berlin, and Göttingen, M.D. Göttingen, 1852, At age 26 Prof. Anatomy and Physiology, Basel 1855; Prof. Physiology and Zoology and Histology, Freiburg i Br. 1857; Prof. Physiology, Göttingen, 1860-1901. With R. Wagner discovered the touch organs in human skin ("Meissner's corpuscles"). Meissner ceased publishing in 1869 after abortive forays into generation of electrochemical potential in biological systems and considerable unproductive studies related to antozone.

18. V. Rothmund, "Über das sogenannte Antozon," *Z. Elektrochem.*, **1917**, 23, 170-173. Viktor Rothmund, 1870-1927. Studied Leipzig, Munich (D. Phil. Munich, 1894). Privatdozent Munich 1898. 1902, Assoc. Prof., 1911 Prof. physics German Un. of Prague; V. Rothmund, "Über das Auftreten von Nebeln bei chemischen Reaktionen," *Monatsh. Chem.*, **1918**, 39, 571-601.
19. S. W. Johnson, "Abstract of Prof. Meissner's Researches on Oxygen, Ozone, and Antozone," *Am. J. Sci. Arts*, **1864**, 87, 325-335. Samuel William Johnson, 1830-1909. Studied with Liebig, also in France, and at Yale Un. Faculty at Yale from 1855, Professor of Chem. 1875. Elected to Natl. Acad. Sci. 1868. Specialized in agricultural chemistry. G. F. Barker, "Abstract of the Second Series of Professor Meissner's Researches upon Electrized Oxygen," *Am. J. Sci. Arts*, **1870**, 100, new series vol 50, 213-223. George F. Barker, 1835-1910. M.D., Albany Med. School, 1863. Prof. physics, Un. Penn. 1872-1900. Pres. Am. Assoc. Adv. Sci., Am. Chem. Soc.
20. L. v. Babo, "Wird neben ozon durch den elektrischen Strom auch sogenanntes antozon erzeugt?" *Ann Chem. Pharm.*, **1863**, II Supp., 291-296. Clemens Heinrich Lambert von Babo, 1818-1899. Professor in Freiburg i Br. M.D. Heidelberg, then to Liebig in Giessen, Habilitation 1845, Freiburg i. Br., 1850 Prof. Chem. in the medical faculty in Freiburg.
21. C. Weltzien, "Ueber das Wasserstoffperoxyd und das Ozon," *Ann. Chem. Pharm.*, **1866**, 138, 129-164. Cf. also "Sur la polarisation de l'oxygène, les ozonides et les antozonides," *Ann. Chim. Phys.*, [3], 1860. Karl Weltzien, 1813-1870, M.D. Heidelberg 1835. With Mitscherlich in Berlin, 1835-1840. Privatdozent 1841, Assoc. Prof. 1842, Prof. 1850 in the Technical Institute of Karlsruhe. Emeritus 1868. Local chairman of the 1860 Karlsruhe Conference.
22. C. Engler and O. Nasse, "Ozon und Antozon," *Ann. Chem. Pharm.*, **1870**, 154, 215-237. Karl Oswald Viktor Engler, 1842-1925. D. Phil. 1864, Freiburg i. Br. 1867 Privatdozent, 1871 Assoc. Prof., 1876 Prof., Halle. In 1887 moved to Karlsruhe, Curator of the Lebensmittel-Prüfungscommission. Member of the Reichstage, 1887-90, active in petroleum research, 1879-1880; wrote a critical review of ozone chemistry.
23. C. B. Fox, *Ozone and Antozone. Their History and Nature*, J. & A. Churchill, London, 1873.
24. A. R. Leeds, "The History of Antozone and Peroxide of Hydrogen," *Ann. N.Y. Acad. Sci.*, **1879**, 1, 405-425. Albert Ripley Leeds, 1843-1902. Prof. Chem. at Haverford College, 1867-1871. From 1871 Professor at Stevens Institute of Technology, Hoboken, N.J. Vice President American Chemical Society. Leeds made limited original contributions to ozone chemistry but set himself up as the arbiter of other investigators' work.
25. M. B. Rubin, "The History of Ozone. III. C. D. Harries and the Introduction of Ozone into Organic Chemistry," *Helv. Chim. Acta*, **2003**, 86, 930-940.
26. C. D. Harries, "Ueber die Einwirkung des Ozons auf organische Verbindungen. (Erste Abhandlung)," *Liebigs Ann. Chem.*, **1905**, 343, 311-375. Carl Dietrich Harries, 1866-1923. Studied at Jena, Munich, and Berlin. D. Phil., Berlin (Tiemann) in 1892. Assistant to A. W. Hofmann at Berlin and, after Hofmann's untimely death that same year, assistant to his successor, Emil Fischer. He rose through all the academic ranks from lecture demonstrator to associate professor. Harries started a research program on ozonolysis. In 1904 he moved as full professor to the University of Kiel. Director of research at Siemens and Halske, 1916-23. A lengthy appreciation of Harries' life and work has been written by R. Willstätter, *Ber. Dtsch. Chem. Ges.*, **1926**, 59, 123-157.
27. C. Harries, "Über die Einwirkung des Ozons auf organische Verbindungen. (Zweite Abhandlung)," *Liebigs Ann. Chem.*, **1910**, 374, 288-368.
28. C. D. Harries, "Über die Einwirkung des Ozons auf organische Verbindungen. (Dritte Abhandlung)," *Liebigs Ann. Chem.*, **1912**, 390, 235-268.
29. C. Harries, "Über die Einwirkung des Ozons auf organische Verbindungen. (Vierte zusammenfassende Abhandlung)," *Liebigs Ann. Chem.*, **1915**, 410, 1-116.
30. C. Harries, *Untersuchungen über das Ozon und seine Einwirkung auf organische Verbindungen*, Julius Springer, Berlin, 1916.
31. Schönbein had originally used the term ozonide for the product of oxidation of inorganic compounds with ozone. The term is used in this sense by inorganic chemists to this day, although the much more common usage is for the addition products of ozone with organic compounds.
32. E. H. Riesenfeld and G. M. Schwab, "Über Ozon," *Ber. Dtsch. Chem. Ges.*, **1922**, 55, 2088-2099.
33. P. Lainé, "Recherches sur l'ozone et ses propriétés magnétiques," *Ann. Phys. [11]*, **1935**, 3, 461-554.
34. E. Bernatek, H. Hagen, and T. Ledaal, "Acidolysis of Some Stable Ozonides," *Acta Chem. Scand.*, **1967**, 21, 1555-1557.
35. G. N. Lewis, "The Magnetism of Oxygen and the Molecule O₄," *J. Am. Chem. Soc.*, **1924**, 46, 2027-2032. Gilbert Newton Lewis, 1875-1946. Ph.D. Harvard (Richards) 1899. Studied with Ostwald and Nernst after his doctorate. Instructor Harvard 1901-04, then spent one year at the Bureau of Science of the Philippine Islands (Manila). Asst. Prof. MIT 1907, Assoc. Prof., 1908, Prof. 1911. In 1912 he went to Berkeley where he was Dean of the College of Chemistry. Among his many contributions: the octet rule, the concept of electron pair and shared electron pair bonds, accurately measured electrochemical potentials of many elements; studied dyes and colored organic substances. Discovered (with Calvin) paramagnetism of free radicals and the phosphorescent state of molecules. Introduced the concepts of activity, fugacity, and ionic strength, was the first to obtain (with Urey) macroscopic quantities of deuterium and D₂O and study their properties. Obtained the first evidence of thermodynamic isotope effects. Many honors, excepting the Nobel prize.

36. D. S. Peterka, M. Ahmed, A. G. Suits, K. J. Wilson, A. Korkin, M. Nooijen, and R. J. Bartlett, "Unravelling the Mysteries of Metastable O₄," *J. Chem. Phys.*, **1999**, *110*, 6095-6098 and references therein. Arthur G. Suits, Ph.D. Berkeley, Prof. Wayne State Un.
37. A. Rieche, R. Meister, and H. Sauthoff, "Über Ozonide und ihre Spaltung," *Liebigs Ann. Chem.*, **1942**, *553*, 187-249. Friedrich Robert Alfred Rieche, 1902-2001. Doctorate at Erlangen in 1925 (Pummerer); then studied microanalysis at Graz under Pregl. Habilitation, Erlangen 1930, published as "Alkylperoxyde und Ozonide: Studien über Peroxydischen Sauerstoff. In 1933 became head of scientific research at the IG Farben dyeworks at Wolfen and Prof. in Leipzig in 1937. After World War II he spent five years in the Soviet Union before returning to Wolfen. In 1952 he resumed his old position and also became Professor and Director of the Institute of Technical Chemistry at the University of Jena. In 1954 he left Wolfen to become the Director of the Research Institute for Organic Chemistry of the (East) German Academy of Sciences at Berlin-Alderhof. Remained in Berlin until his death in 2001 (age 99). Baeyer medal, Kekulé Medal.
38. G. Osann, "Ueber eine Modification des Wasserstoffs," *J. Prakt. Chem.*, **1853**, *58*, 385-391. Gottfried Wilhelm Osann, 1797-1866. Privatdozent in physics and chemistry Erlangen, 1819, Jena 1821. 1823-28 Professor of Chemistry and Pharmacy, University of Dorpat. 1928, Prof. of Physics and Chemistry, Würzburg. Collaborated with Berzelius and made a preliminary identification of the element ruthenium.
39. G. Osann, "Ueber active Modificationen des Sauerstoffs und des Wasserstoffs," *J. Prakt. Chem.*, **1854**, *61*, 500-503; G. Osann, "Ueber bemerkenswerthe chemische Eigenschaften des auf galvanischem Wege ausgeschiedenen Sauerstoff- und Wasserstoffgases," *J. Prakt. Chem.*, **1855**, *66*, 102-117; G. Osann, "Den Ozon-Wasserstoff betreffend," *Ann. Phys. Chem.*, **1856**, *98*, 181-183; G. Osann, "Neue Versuche über die verschiedenen Zustände des Wasserstoffgases," *J. Prakt. Chem.*, **1856**, *69*, 1-10; G. Osann, Weitere Versuche, welche die Verschiedenheit des galvanisch ausgeschiedenen Wasserstoffgases gegen das gewöhnlich dargestellte darthuen," *Ann. Phys. Chem.*, **1856**, *173*, 327-328; G. Osann, "Neue Versuche über den ozon-wasserstoff," *Ann. Phys. Chem.*, **1857**, *71*, 355-360; G. Osann, "Ueber die reducirende Wirkung des elektrolytisch ausgeschiedenen Wasserstoffgases," *Ann. Phys. Chem.*, **1855**, *171*, 311-315; G. Osann, "Neue Thatsachen in Betreff der Eigenthümlichkeit des auf galvanischem Wege dargestellten Wasserstoffgases," *Ann. Phys. Chem.*, **1855**, *171* (76), 315-319; G. Osann, "Erwiderung auf die Einwendungen, welche gegen meine Untersuchung über den Ozon-Wasserstoff erhoben worden sind," *J. Prakt. Chem.*, **1864**, *92*, 210-213.
40. W. B. Jensen, "What Ever Happened to the Nascent State?" *Bull. Hist. Chem.*, **1990**, *6*, 26-36. See URL Ref. 1. William Barry Jensen, 1948-. B.S. Wisconsin 1970, M.S. 1972, Ph.D. 1982. Asst. Prof. Rochester Inst. of Tech. 1983-86. Oesper Prof. Hist. of Chem and Chem. Educ. Un. of Cincinnati. Founding editor *Bull. Hist. Chem.*
41. W. Hisinger and J. J. Berzelius, "Expériences galvaniques," *Ann. Chim.*, **1804**, *51*, 167-174. William Hisinger, 1766-1852, wealthy mine owner.
42. J. R. Partington, *A History of Chemistry*, Macmillan, London, Vol. 4, **1961-7**, 120.
43. G. Magnus, "Ueber directe und indirecte Zersetzung durch den galvanischen Strom," *Ann. Phys. Chem.*, **1858**, *104*, 553-580. Heinrich Gustav Magnus, 1802-1870. D. Phil. Berlin (Mitscherlich), 1827. In Paris 1828-9. Traveled to England with Wöhler, spent a year with Berzelius. Un. of Berlin, Privatdozent 1831, Assoc. Prof. 1834, Prof. of Physics and Technology 1845. Many original contributions including studies of platinum complexes, discovery of polymerization of hydrocarbons, discovery of periodic acid and its salts, behavior of oxygen and carbon dioxide in blood, studies of gas behavior, electrolysis, etc. John Dean, probably D. Phil. Göttingen (Wöhler). Later practiced medicine in Waltham., MA, USA.
44. J. J. Thomson, "Bakerian Lecture - Rays of Positive Electricity," *Proc. R. Soc. London A*, **1913**, *89*, 1-20. Sir Joseph John Thomson, 1856-1940. D.Sc. Dublin. 1880, Fellow Trinity Coll. Cambridge 1883, lecturer 1884, Cavendish Prof of Exptl. Physics. 1894 President Cambridge Pphilosophical Society. 1884 FRS. 1916-20 Pres. Royal Soc. Nobel prize in physics 1906. Many honorary doctorates including Oxford, Dublin, Columbia. Discovered electron, mass spectrometry, isotopes.
45. A. J. Dempster, "Ionization and Dissociation of Hydrogen Molecules and the Formation of H₃," *Philos. Mag. (III)* **1916**, *31*, 438-443. Arthur Jeffrey Dempster, 1886-1950. B.S. 1909, M.S. 1910, Un. of Toronto, Ph.D. Physics, Un. of Chicago, 1916; physics faculty, 1916-. Chief physicist Un. Chicago Metallurgical Lab., 1943-46. Division Director Argonne National Lab, 1946-50. Developed first modern mass spectrometer in 1918, discovered U-235 in 1935.
46. H. M. Smallwood and H. C. Urey, "An Attempt to Prepare Triatomic Hydrogen," *J. Am. Chem. Soc.*, **1928**, *50*, 620-626 and references therein. Hugh Molleson Smallwood, 1903-1953. B.S. John Hopkins Un., 1924, Ph.D., 1927. Instructor 1927-29, Harvard. U. S. Rubber Co. 1929-1953. Harold Clayton Urey, 1893-1981. B.S. Montana, 1917, Instr. Montana 1919-21; Ph.D. Un. Cal., 1923. Am. Scand. Found. Fellow, Copenhagen, 1923-4. Assoc. in Chem. Hopkins 1924-29. Assoc Prof. Columbia Un., 1929-1934, Prof. 1934-. Editor, *J. Chem. Phys.*, 1933-. Member of Staff Inst. of Nuclear Studies, Un. of Chicago, 1945. Nobel Prize 1934.
47. G. Herzberg, "The History of the Discovery of the Spectra of CH₂ and H₃," *J. Mol. Struct.*, **1990**, *217*, xi-xviii. Gerhard Herzberg, 1904-1999. Dr. Eng. Physics, TH Darmstadt 1928 (Rau). Postdoctoral studies Göttingen, Bristol (1928-30). Escaped from Germany to Canada. 1935, Guest Prof. Un. Saskatchewan. Prof. Physics,

Saskatchewan 1936-45. Prof. Spectroscopy, Yerkes Observatory, Un. of Chicago, 1945-48. Director Div. of Pure Physics, Natl. Res. Council of Canada 1948-1969; Distinguished Research Scientist, Natl. Res. Council of Canada, 1969. Nobel Prize Chem. for contributions to electronic structure and geometry, 1971. Chancellor Carleton Un., Ottawa 1973-80.

48. E. Breitmaier, "No Enantioselective Reactions in a Static Magnetic Field," *Angew. Chem. Int. Ed. Engl.*, **1994**, 33, 1207.

ABOUT THE AUTHOR

Mordecai B. Rubin has been emeritus professor of chemistry at the Schulich Faculty of Chemistry, Technion, Haifa since 1994. He can be contacted at chrubin@tx.technion.ac.il. Retirement is like a permanent sabbatical if one can remain healthy. He did some work with ozone in his postdoctoral incarnation and ozone has been the companion of his later years. Three atoms can combine into a plethora of chemistry.

Editor's Note: The Scheme below was inadvertently omitted from the previous paper on ozone, ["Ozone VI.,"] which appeared in the *Bulletin*, **2008**, 33, 68-75. My sincere apologies to the author, M. Rubin.

