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EARLY CONTRIBUTIONS TO THE CHEMISTRY OF ORGANIC RADICAL IONS

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Abstract—The correct chemical composition and the true nature of organic radical ions were not recognized until well into the 20th century. Yet, the earliest observation of such a species as a colored transient dates back at least 150 years. Some pioneering reactions involving radical ions are discussed, and contributions to their understanding are reviewed.

Organic radical ions are recognized today as important intermediates in many areas and they have been discussed in advanced or even elementary organic chemistry texts for decades. However, the concept of an intermediate with both unpaired spin and charge was not appreciated until after the recognition of trivalent carbon by Gomberg[1] and was not generally accepted until well after free radicals.

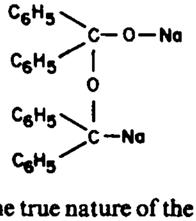
We use this issue as an opportunity for a look at some pioneering experiments which we consider early contributions to the organic radical ion field. The earliest formed organic radical cation probably was the molecular ion of methane, generated in a planetary (Iovian) atmosphere by solar irradiation aeons ago. The first incidents of radical cation generation in the laboratory and of their subjective observation as colored transients date back well over 100 years. Yet, the true nature of these intermediates was elucidated only 60 years ago and generally accepted even more recently. The first radical anions were produced and perhaps observed 150 years ago; they were approached in a systematic fashion some 50 years later; and their structure was recognized 75 years ago.

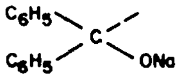
The history of organic radical ions is intertwined with the history of "quinhydrones", molecular aggregates between substrates that are readily oxidized and compounds that are readily reduced. In the absence of modern analytical methods, particularly magnetic ones, it was often difficult to ascertain whether one was dealing with a homogeneous radical ion salt or with a quinhydrone. Indeed, in several instances radical ions were mistaken for molecular complexes. On the other hand, there are instances where a radical ion and a molecular complex have a similar appearance, at least subjectively, so that it is not clear which of the two species was observed originally.

As a case in point, we mention work of Laurent in Paris, carried out and published in 1835. He was successful in preparing benzil from the oil of bitter almonds.[2] Of course, neither the quadrivalence of carbon nor its proper atomic weight were known at the time. Therefore, the compound was identified as the "radical" benzoyl and its composition was given as $C_{28}H_{10}O_2$, a substance whose existence Liebig and Wöhler had postulated four years earlier.

Laurent treated the new compound with potassium tartrate and observed a "rose colored solution". One might be inclined to assume that this reaction leads to the semidione in analogy to the formation of semiquinones under similar conditions. However, Scholl showed in 1899 that the color reaction requires the presence of some benzoin,[3] an impurity which Laurent might have overlooked. Accordingly, the colored species should be a quinhydrone and it was identified as such by Weissberger *et al.*[4]

Laurent also reacted benzil with potassium and observed spontaneous ignition. Under appropriate conditions this reaction would have given rise to the first radical anion. Some 50 years later, similar experiments were carried out more successfully by Beckmann and Paul in Ostwald's laboratory in Leipzig.[5] These workers reacted aromatic ketones (benzophenone) and diketones (benzil) with sodium in order to evaluate the nature of the bond between the metal atom and the carbonyl moiety. Because of the sensitivity of the solutions and the colored solid products to air and moisture, they worked in a hydrogen atmosphere. The apparatus designed for these experiments (Fig. 1) documents quite a respectable state of the laboratory art for its day. The products obtained upon quenching the isolated solid with water or with carbon dioxide followed by water led to a formulation of the reaction intermediate as a dimer with an oxygen bridge.





The true nature of the intermediates was recognized 20 years later by Schlenk and co-workers.[6,7] They clearly understood that the reaction of alkali metals with ketones may involve different pathways, including the formation of dimeric ketyls, the most frequently invoked alternative structure type. However, they established that several of the colored reaction products had unique properties and suggested that they constitute a new class of trivalent-carbon compounds.[6] They considered the intense color and extreme air sensitivity as characteristic properties of these species and identified the reaction with oxygen followed by hydrolysis as one producing hydrogen peroxide. Schlenk proposed the term "metal ketyls" to represent the compostion and (by the suffix "yl") the "radical nature" of these substances. It appears that Schlenk and his co-workers understood the salient features of these radical anions. However, their interpretation was not readily accepted. Particularly the ready transformation of sodium benzophenone

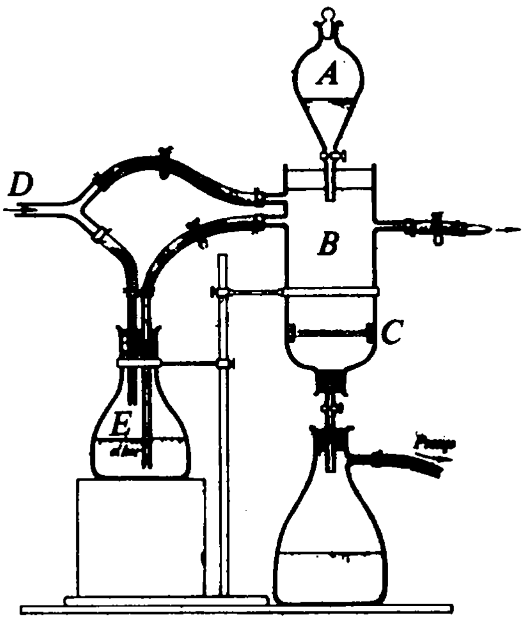
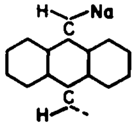


Fig. 1. Apparatus for the reaction of alkali metals with carbonyl compounds and for the separation of the solid adducts (adapted from Beckmann and Paul[5]). A, separatory funnel in which the reaction is carried out; B, cylinder with inert atmosphere; C, perforated porcellain disc with filter paper, held in place by cork rings; D, entry of inert gas (H_2 or CO_2) from Kipp apparatus; E, wash ether reservoir.

to the corresponding pinacol, which had been noted already by Beckmann and Paul, led to the continuing formulation of the radical ion as dimeric ketyl. It would take the combined information provided by conductivity[8] and magnetic susceptibility measurements[9,10] in the 1930s and electron spin resonance since the 1950s to fully reveal a complex system in which radical anions, dissociated or paired with an alkali metal ion, and (dimeric) pinacolate ions play prominent roles.

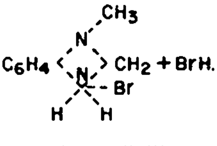
As for the radical anions of aromatic hydrocarbons, one prototype may have been involved as early as 1866, when Berthelot reacted naphthalene with potassium.[11] The reaction proceeded without the evolution of hydrogen and led to a black, solid dipotassium salt "$C_{20}H_8K_2$". Once again, the assumed number of carbon atoms reflects the incorrect atomic weight for carbon. Depending on the medium and on the rate of addition, this reaction might have involved the naphthalene radical anion as a more or less fleeting intermediate. However, the highly delocalized radical anions of aromatic hydrocarbons presented a puzzle that would remain unsolved for another 50 years. Berthelot's findings, and their potential significance, were unappreciated.

Nearly 50 years later Schlenk and co-workers extended their work on metal ketyls[6,7] to a systematic study of the interaction between hydrocarbons and sodium and found evidence for many disodium dianions.[12] In the case of anthracene they noticed the existence of two different species, the purple dianion and a blue, transient species with a banded spectrum. They identified this intermediate as a "monosodium addition product which contains trivalent carbon". This description captures the essence of the structure, although details such as the spin density distribution or the association with the alkali counterion would be revealed only in electron paramagnetic resonance experiments.

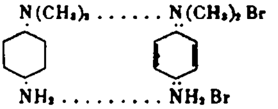


As for organic radical cations, we suggest that one of the first examples to be observed in the laboratory was that of a *p*-phenylenediamine derivative. In 1875, Baeyer, then still in Strassburg, presented a progress report about work on aromatic nitroso compounds which he had begun with Caro.[13] This project would lead Caro to the synthesis of methylene blue, whereas several years later in Baeyer's München laboratory it would yield the colored radical cation salts of Wurster. In the third section of Baeyer's 1875 report, Schraube deals with the preparation of dimethyl-*p*-phenylenediamine by reduction of the corresponding nitroso compound. Schraube noted that the impure solid showed a reddish color.[14] This report prompted Weber, a Zürich doctoral student, to publish his own findings on the same subject. He reported that in solutions of the diamine "weak oxidizing agents such as aqueous ferric chloride ... cause an intense, beautiful red to violet color".[15]

After Baeyer's move to München, he suggested to several associates the further study of *p*-phenylenediamine derivatives.[16–19] In the course of these investigations, Wurster succeeded in isolating colored salts from dimethyl- and tetramethyl-*p*-phenylenediamine. He recognized that the colors were due to oxidation products, and that the oxidation was readily reversible. He also noted that the salts contained only one equivalent of acid. In summarizing his findings he proposed the following structure, i.e. he rationalized the color by the net substitution of bromine for hydrogen and by a rearranged structure.



Almost 30 years later Willstätter and Piccard resumed the investigation in Zürich and contributed some relevant details.[20] They determined that the oxidation with one equivalent of bromine results in maximum coloration and that the second equivalent leads to the colorless quinonediimine. Accordingly, they called Wurster's salts "halbchinoid" (meriquinoid) and their oxidation products "ganz chinoid" (holoquinoid). They observed furthermore that the colored compounds could be obtained by mixing equimolar amounts of phenylenediamine and quinonediimine. This may have led them to formulate the colored salts as molecular aggregates with specific N···N bonds. Piccard would write in 1913 (when he was an associate of Baeyer in München): "Since the typical properties of meriquinoid salts (intense color, banded spectra, stability against water and alcohol, ...) are tied to the presence of amino or imino groups, Willstätter and Piccard have assumed that the valences uniting these molecules originate in the nitrogen atoms of the effective groups ..."[21]



Other aromatic radical cation salts have a similar history and were also considered to be molecular complexes. For example, the thiophenazine radical cation was observed originally in the early 1880s. Following the preparation of methylene blue by Caro and of a purple analog by Lauth,[22] Bernthsen attempted to clarify the chemical nature of these compounds.[23-26] He demonstrated the close relationship of the two dyes and was able to synthesize the unsubstituted prototype, phenothiazine. He noted that the new product was readily oxidized leading to red or green solutions depending on the reaction conditions. The oxidation products were understood as "addition compounds".

Thirty years later, Kehrmann and co-workers[27,28] were able to show that the oxidation proceeds in two steps: "the direct oxidation of thiodiphenylamine with bromine, iron chloride, or cold concentrated sulfuric acid" leads to "semiquinoid salts". They characterized two series of salts, semiquinoid and holoquinoid, "by subjective and spectroscopic" observation. However, as Willstätter and Piccard in the case of Wurster's salts, Kehrmann and Diserens considered the meriquinoid salts molecular complexes consisting of "one molecule phenazthionium with one molecule thiodiphenylamine and one molecule of hydrogen bromide".

The fact that both Willstätter and Kehrmann invoked molecular complexes, albeit of different nature, as structures for the radical cation salts, is probably due to the emergence of such complexes at the time. Werner had found colored adducts between aromatic hydrocarbons and nitro compounds,[29] whereas Haakh had observed similar adducts between hydrocarbons and quinones.[30] However, in the case of Wurster's and of the thiophenazonium salts the description as donor–acceptor complexes is, of course, incorrect.

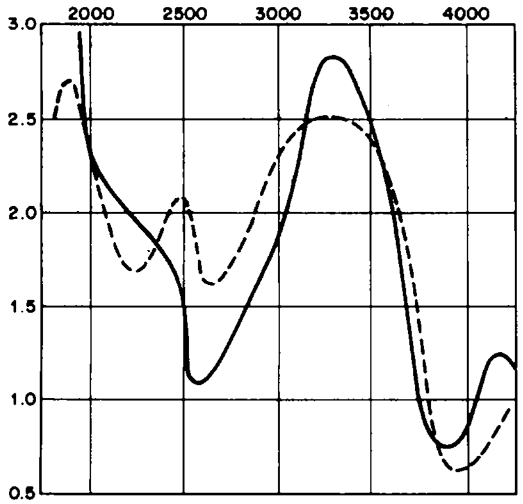
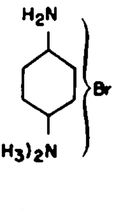


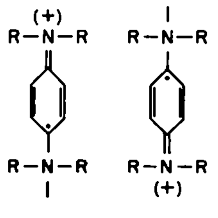
Fig. 2. Optical spectra of "holoquinoid" (—) and "meriquinoid" (---) N-methyl-phenazonium ions in ethanol (adapted from Hantzsch[31]).

We suggest that Hantzsch may have been the first to recognize the common features of several radical cation salts.[31] At the time he was involved in an acrimonious polemic with Kehrmann concerning "chromo-isomerism" in phenazonium salts. In his final paper on the subject in 1916, he raised the possibility, that... "these salts are not at all molecular complexes, but uniform, monomolecular chemical compounds with an unsaturated nitrogen or sulfur atom, whose unsaturated state would explain the intense color...". In support of this interpretation he showed that the spectral changes (Fig. 2) between holo- and meriquinoid states for phenazonium, thiophenazonium, thianthronium, and Wurster's salts are quite different from those between quinones and quinhydrones. Although there is no reference to an unpaired spin or the delocalization of spin and charge, we consider Hantzsch's description a milestone in the understanding of these radical cations.[31]

A decade later, Weitz may have been the first to understand the true nature of Wurster's salts (and, indeed, of many additional cationic and anionic species).[32] In this 1928 paper "Zur Theorie der Chinhydrone" he expressed the view that many of these species are monomolecular and contain an unpaired electron. Indeed, he called them "Anionradikale" and "Kationradikale". "Both the salt and the cation have an odd number of electrons because of their radical-like composition." Concerning the bonding to the anion he stated "... the anion ... should belong to both amino (or ammonium) groups (but should not be bound to them) so that the single positive charge is distributed between both halves of the cation ...". He represented this type of association by the structure shown below. It is also interesting to note that he considered "... this strange charge distribution ..." to be "... the cause of the deep color ...". Although some of the terminology used by Weitz may be unfamiliar to today's chemists, and although the spin density distribution suggested by the above formulae does not quite correspond to that established today, there is no doubt that he understood the nature of the *p*-phenylene diamine radical cations.



Weitz, 1928



Michaelis, 1935

In the 1930s the application of potentiometric methods promoted a deeper understanding of these species. Michaelis compared the reactivities of these

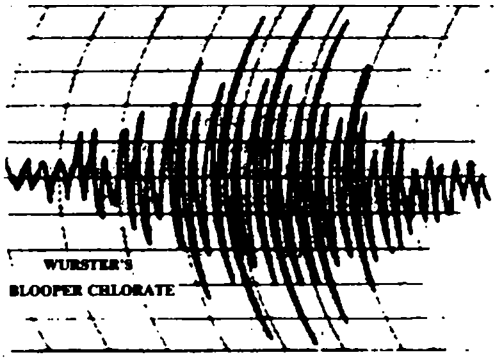


Fig. 3. Electron paramagnetic resonance spectrum of Wurster's blue ion (adapted from Weissman *et al.*[35]).

radical cations with those of trivalent-carbon or divalent-nitrogen intermediates and ascribed their unusual stability to "resonance". "The fact that such radicals are capable of existence at all, can be attributed to a particular symmetry of structure resulting in resonance." He proposed that a number of "limiting states" contributed "a share to the resonating or mesomeric state". The structures he deemed most important are shown above. Michaelis provided the explanation that "letters are atomic kernels, dashes are pairs of elecrons, ... and the dot is a single electron". He realized that the entire molecule had to be planar for an effective delocalization.[33,34]

Later experiments bore out Michaelis' assignment. Wurster's blue became an early target for EPR investigation and it was one of the earliest organic free radicals for which hyperfine splitting was observed (Fig. 3).[35] The tetramethyl derivative became the first system in which the degenerate electron transfer between an organic free radical and its diamagnetic precursor was studied successfully by NMR line broadening.[36,37]

With the advent of electron paramagnetic resonance several classes of relatively stable radical ions became accessible to detailed investigation, among them ketyls, semidiones, semiquinones, and the one-electron reduction and oxidation products of numerous aromatic systems.[40] The development of the McConnell relation made it possible to interpret the hyperfine coupling patterns of the paramagnetic intermediates in terms of the electron spin density distribution throughout the molecule,[41,42] providing a most sensitive probe into the electronic structure. These developments raised the radical ion field to a new level of understanding and laid the foundation for the progress and the new advances of the last 20 years.

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