ities underlying the correlation of yield with the kind of organic halide used.

Ames, Iowa

---

[Contribution from the Chemical Laboratory of Harvard University]

# THE FORMATION OF FREE RADICALS BY REDUCTION WITH VANADOUS CHLORIDE

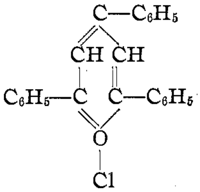
## Preliminary Paper

By J. B. Conant and A. W. Sloan

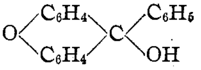
Received August 3, 1923

The addition of vanadous chloride to a solution of triphenylpyrylium chloride (I) causes the formation of a reddish precipitate which can be obtained in a fairly pure condition by filtering in an atmosphere of carbon dioxide. This colored, insoluble substance behaves like a free radical; a chloroform solution of it is bright red and the color disappears when the solution is shaken with air. The substance is reoxidized to the pyrylium salt by ferric chloride; if this process is carried out quantitatively in the absence of oxygen a maximum of one molecule of ferric chloride is required. Considerably less than this amount suffices to oxidize a precipitate which has stood for some hours even in an atmosphere of carbon dioxide; the compound is apparently unstable.

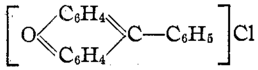
While these facts clearly indicated that we were dealing with a free radical, we desired to obtain still more positive evidence. We, therefore, investigated the reduction of the salts of phenylxanthenol (II) from the chloride of which Gomberg[1] obtained the free radical phenylxanthyl by the action of metals in benzene solution. Phenylxanthenol dissolves to a slight extent in concd. hydrochloric acid, producing an orange-colored solution. This solution presumably contains a chloride for which the oxonium formula (III) can be written. This salt is much more readily hydrolyzed than the pyrylium salt, so that it is necessary to work with concd. hydrochloric acid solutions. When such a solution of phenylxanthylium chloride is treated with vanadous chloride a brown precipitate



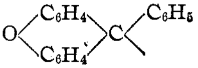
(I)



(II)



(III)



(IV)

---

[1] Gomberg and Cone, *Ann.*, **370**, 154 (1909).

is formed which is very similar in its reactions to the substance formed by the reduction of triphenylpyrylium chloride. It dissolves in chloroform or benzene giving a red solution which to the eye seems identical with solutions of phenylxanthyl (IV) prepared according to Gomberg's procedure. Furthermore, on shaking these solutions with air a peroxide is formed identical with the peroxide formed by oxidation of phenylxanthyl. There is, therefore, no doubt that vanadous chloride reduces phenylxanthylium chloride to phenylxanthyl, and there is every reason to believe that from triphenylpyrylium chloride a corresponding free radical is formed.

This novel type of reduction is not confined to oxonium salts. The so-called carbonium salts of triphenylcarbinol are reduced by vanadous salts to triphenylmethyl. Triphenylcarbinol is slightly soluble in a very concentrated aqueous solution of zinc chloride saturated with hydrogen chloride; a colored precipitate is formed on adding vanadous chloride to this solution. The existence of triphenylmethyl in this precipitate was demonstrated both by the color of a benzene solution and by the isolation of the peroxide obtained on shaking the solution with air. A solution of triphenylcarbinol in concd. sulfuric acid is also reduced by vanadous chloride, a precipitate containing triphenylmethyl being formed.

In this preliminary paper we shall not enter into a discussion of the much debated subject of the constitution of salts of triphenylcarbinol[2] nor of the relative advantages of the oxonium or carbonium formulas for the pyrylium and xanthylium compounds.[3] For our present purposes we may consider that *in solution* the "oxonium" and the "carbonium" salts are present, at least to some extent, as polar compounds; if this is so, the reduction of such salts to free radicals is comparable to the reduction of stannous chloride to metallic tin by the action of chromous chloride. These processes appear to be reversible and to consist essentially of the gain or loss of an electron from a certain group of atoms which can function either as a positive ion or as a free radical, thus: $(C_6H_5)_3C^+ + E \rightleftharpoons (C_6H_5)_3C—$.

Recent investigations have shown that a number of reversible organic processes which can be formulated in terms of electronic transfer give definite potentials.[4] Preliminary experiments indicate that reduction potentials of certain organic salts to free radicals can also be measured; such potentials of free radicals are analogous to the single potentials of

---

[2] See Hantzsch [*Ber.*, **55**, 953 (1922)] for one of the recent papers on this subject.

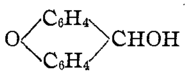
[3] Gomberg and West, THIS JOURNAL, **34**, 1529 (1912). Gomberg and Cone, *Ann.*, **376**, 183 (1910).

[4] (a) Haber and Russ, *Z. physik. Chem.*, **47**, 257 (1904). (b) Granger and Nelson, THIS JOURNAL, **43**, 1401 (1921). (c) Clark, *J. Wash. Acad. Sci.*, **10**, 255 (1920). (d) Biilmann and Lund, *Ann. chim.*, **16**, 321 (1921). (e) Conant, Kahn, Fieser and Kurtz, THIS JOURNAL, **44**, 1382 (1922). (f) LaMer and Baker, *ibid.*, **44**, 1954 (1922). (g) Conant and Fieser, *ibid.*, **44**, 2480 (1922).

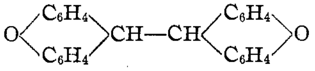
the metals. We hope to deal with this subject in more detail in another paper.

## Free Radicals and Bimolecular Reduction

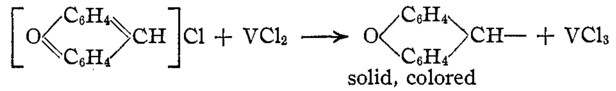
The extensive work of Gomberg and others on free radicals has shown that the so-called free radical is in solution an equilibrium mixture of the monomolecular free radical and its bimolecular association product. In the case of triphenylmethyl the following equation represents one of the equilibria which are involved (we will neglect in this discussion the tautomeric equilibria involving color changes). $2(C_6H_5)_3C^- \rightleftarrows (C_6H_5)_3C-C(C_6H_5)_3$. The extent of the dissociation of the bimolecular form is a function of the nature of the groups attached to the central carbon atom. This being the case, one would expect that in many cases in which "onium halides" were reduced to radicals the free radicals would polymerize completely to the associated form; if this associated form was not appreciably dissociated in the solution, simple bimolecular reduction would apparently have occurred. However, if the first reduction product should separate rapidly in the solid form before it had wholly associated it might be possible to obtain a solid "free" radical whose existence in solution could not be demonstrated. We believe that we have realized such a case in the reduction of the salts of xanthenol (V) with vanadous chloride. When a very dilute solution of xanthenol in concd. hydrochloric acid is treated in the cold with vanadous chloride a pink precipitate is immediately formed. This can be filtered off and is stable for a few hours in the air but gradually becomes colorless. The colorless solid is bixanthyl[5] (VI). When the bright pink precipitate is washed with water, sucked dry and then dissolved in chloroform in the absence of air (in a special apparatus) a momentary color is produced in the chloroform which fades in a few seconds. The chloroform solution on evaporation yields bixanthyl. This color change is a strong indication that the solid which is precipitated on the addition of vanadous chloride contains some "free" xanthyl radical (VII) which dissolves in chloroform with a brown color and then immediately and completely polymerizes to the colorless bixanthyl. If our interpretation of these color changes is correct a new method is available for mak-


$O\left\langle\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\right\rangle CHOH$

(V)

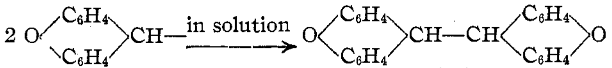

$O\left\langle\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\right\rangle CH-CH\left\langle\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\right\rangle O$

(VI)


$\left[O\left\langle\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\right\rangle CH\right]Cl + VCl_2 \longrightarrow O\left\langle\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\right\rangle CH- + VCl_3$

solid, colored

(VII)


$2\,O\left\langle\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\right\rangle CH- \xrightarrow{\text{in solution}} O\left\langle\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\right\rangle CH-CH\left\langle\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\right\rangle O$

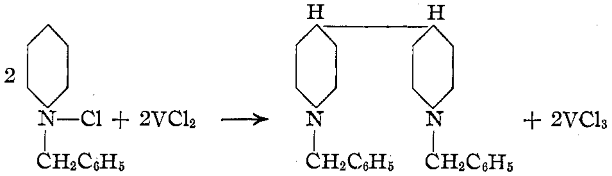
colorless

---

[5] Fosse, *Bull. soc. chim.*, [3] **35**, 1005 (1906).

ing solid organic radicals which are not free in solution. We are now investigating the extension of this method as well as the closely allied problem of the reduction of various types of aldehydes and ketones with vanadous and chromous salts.

The reduction of pyridinium and acridinium salts should be entirely analogous to the reduction of pyrylium and xanthylium compounds. Indeed, Cone showed some years[6] ago that by the action of metallic zinc on an aqueous solution of N-phenyl-phenylacridinium chloride a free radical was formed. This reaction can be formulated either as the general reaction between a metal and the solution of an organic chloride giving a free radical or as a case of reduction brought about in this case by a metallic reducing agent. There is one difference between the reduction of pyrylium and pyridinium compounds: the reduction products of the former series whether as free radicals or in the bimolecular form no longer have basic properties; they therefore precipitate from acid solution on the addition of vanadous chloride. This would not be the case with the nitrogen compounds, since even in the reduced form the trivalent nitrogen would have basic properties. It is, therefore, not surprising that on the addition of vanadous chloride to benzylpyridinium chloride (VIII) there is no apparent change; on making the solution alkaline, however, and extracting with ether, the bimolecular reduction product, N′,N-dibenzyl-tetrahydrodipyridyl (IX), is obtained. By analogy with the carbonium compounds there is every reason to believe that the first step in the process is the formation of the free radical, benzylpyridinium,[7] but since this is soluble in the acid solution it immediately polymerizes to the bimolecular form.



(VIII) (IX)

If we formulate the relationship between a free radical and the corresponding "onium salt" in terms comparable to the single electrode potential of a metal, it is obvious that all reducing agents whose potentials are below the potentials of the free radicals should cause the precipitation of the radical. In the case of those compounds which we have so far investigated, vanadous chloride has a sufficiently low potential (normal potential about —0.200 referred to hydrogen) to cause this reaction; titanous salts (about —0.040) do not cause a rapid reduction. Chromous

[6] Cone, THIS JOURNAL, **34**, 1695 (1912); **36**, 2101 (1914).

[7] Weitz, [*Ann.*, **425**, 202 (1921)] and Emmert [*Ber.*, **53**, 370 (1920)] reported that they had obtained this free radical, but later [*Ber.*. **55**, 2322, 2864] showed conclusively that the colored substance was bimolecular.

chloride (—0.400) reduces the substances in question to free radicals just as does vanadous chloride, but because of its relative stability we have preferred to use the latter reagent. If too powerful a reducing agent be employed in such a process the free radical may be further reduced to the hydrogen compound, just as arsenic and antimony may be reduced to their hydrides. As in inorganic chemistry, the solubility and dissociation of the various factors and products in an electrochemical reaction are quite as important as the value of the normal potentials. Until we have such information, together with the potentials of the free radicals, it is profitless to pursue further the electrochemical aspects of these reactions.

## Experimental Part

**Reduction of 2,4,6-Triphenylpyrylium Chloride.**—The ferric chloride double salt of this chloride was prepared according to the method of Dilthey[8] and from it the pseudo base and the iron-free chloride. Both the chloride and the ferric chloride double salt are reduced by vanadous chloride in the same manner, except that with the latter compound a certain amount of vanadous chloride is used up in reducing the ferric to ferrous salt. Because the ferric salt is more conveniently prepared it was used in most of the experiments of which the following is typical.

One g. of the ferric chloride double salt was dissolved in 125 cc. of air-free water in a 200cc. Erlenmeyer flask. The flask was swept out with carbon dioxide and 0.1 *N* vanadous chloride added from a buret while the flask was constantly shaken. A reddish solid soon began to precipitate; vanadous chloride was added in excess (until no further precipitate formed). The mixture was then filtered through a Gooch funnel in an atmosphere of carbon dioxide and washed with air-free water.

The red-brown solid thus obtained dissolved in chloroform or benzene with a red color; when shaken with air the solution became colorless or yellow. When suspended in water and treated with ferric chloride solution the brown solid went into solution rapidly and the characteristic yellow double salt of pyrylium chloride and ferric chloride separated on the addition of hydrochloric acid. Several attempts to dry the precipitate in an atmosphere of carbon dioxide were unsuccessful, either because of failure to exclude air completely or because the compound slowly decomposed; the resulting solid was a mixture of yellow and blackish materials which did not show the characteristics of the original compound.

A number of quantitative experiments were carried out in which the precipitate after it was washed was oxidized with ferric alum in an atmosphere of carbon dioxide either with or without the addition of a little benzene to facilitate the solution. After the solution had been thoroughly shaken for 5 minutes the excess of ferric salt was titrated with standard titanium chloride using ammonium thiocyanate as an outside indicator. The following summarizes the results which are very variable but indicate

---

[8] Dilthey, *J. prakt. Chem.*, **94**, 65 (1916).

that one equivalent of hydrogen is involved as a maximum. The figures represent moles of ferric salt required to oxidize the precipitate formed from one mole of double salt: (1) freshly precipitated, 0.92, 0.74, 0.59, 1.00; (2) after 14 hours in carbon dioxide, 0.50; (3) after 3 days in carbon dioxide, 0.29.

**Reduction of 9-Phenylxanthylium Chloride.**—Half a gram of 9-phenylxanthenol was dissolved in 20 cc. of concd. hydrochloric acid and 5 cc. of water by gently warming the mixture. The resulting orange-colored solution was cooled, filtered from a very small amount of insoluble material by means of glass wool and placed in a separatory funnel filled with carbon dioxide. An excess of 0.1 *M* vanadous chloride was run in and a brown precipitate was immediately formed. Chloroform (about 20 cc.) was then added and the mixture shaken; the heavy precipitate completely dissolved, imparting a deep red color to the chloroform. This solution was then run into another vessel and shaken with air; the color rapidly vanished. On evaporation of the chloroform a white solid was obtained which was freed from a small amount of oily material by washing it with ether. It melted sharply with decomposition at 208–209° and weighed 0.25 g. Recrystallized from benzene, it melted at 211° and was identified as phenylxanthyl peroxide by comparison with a sample prepared according to Gomberg's procedure.

**Reduction of Triphenylcarbinol.**—A solution of 0.2 g. of triphenylcarbinol in a mixture of 5 cc. of concd. hydrochloric acid and 10 cc. of zinc chloride solution (100 g. in 50 cc. of water) saturated with hydrogen chloride at a temperature of 70–80°, was cooled and filtered through glass wool; vanadous chloride was added to it in an atmosphere of carbon dioxide. A reddish precipitate was formed which was rapidly filtered off and dissolved in benzene in the absence of air. A brown solution was formed, the color of which was discharged by shaking with air. The benzene solution on spontaneous evaporation yielded a small amount of white solid, insoluble in ether, which melted sharply to a red melt at 180–182° (triphenylmethyl peroxide melts at 185–186°). A solution of 0.5 g. of triphenylcarbinol in 20 cc. of 95% sulfuric acid was treated with vanadous chloride solution; a red precipitate formed. The evolution of hydrogen chloride somewhat hindered the carrying out of this reaction; we propose to use vanadous sulfate for such reactions in future work. The sulfuric acid suspension of the reddish precipitate was poured onto cracked ice and the mixture filtered as soon as the ice had melted. The precipitate dissolved in benzene with the development of color; the color disappeared when the solution was shaken with air and the peroxide was obtained by evaporating the benzene solution and treating the residue with ether.

**Reduction of Xanthylium Chloride.**—A solution of 2 g. of xanthenol in 50 cc. of concd. hydrochloric acid saturated with hydrogen chloride at 0° was filtered from a small amount of material by passing it through glass wool. The light brown solution was treated with an excess of vanadous chloride in the usual manner and the resulting precipitate rapidly filtered in the air and washed with water. A pink solid was thus obtained; attempts to dry it in nitrogen without loss of color were unsuccessful. Recrystallized from acetone after it had become colorless it yielded 1.3 g. of bixanthyl[5] (m. p., 204–205°) and 0.2 g. of oily material. In another experiment the precipitate was immediately dissolved in chloroform, the chloroform solution showing a faint red color for a few seconds and then becoming colorless. Bixanthyl was obtained in a good yield from this solution. To ascertain whether or not the rapid fading of the color of the solution was due to oxidation, the solution in chloroform was carried out in the absence of air. Some of the freshly precipitated compound was placed in one leg of a wide Y-tube and chloroform placed in the other leg. The apparatus was then repeatedly evacuated and filled with nitrogen (free from oxygen). The tube was then tilted and the chloroform rapidly run onto the precipitate which dissolved with a momentary red color, forming after a few seconds a colorless solution. This is strong evidence that the color change was not due to oxidation but to polymerization.

**Reduction of Benzylpyridinium Chloride.**—A solution of 2 g. of benzylpyridinium chloride in 50 cc. of water was treated with 50% more than the amount of vanadous chloride equivalent to two hydrogen equivalents. No precipitate formed but the vanadous chloride was evidently oxidized, as the first portion of it rapidly changed color. The solution was made strongly alkaline and the solution containing a suspension of inorganic hydroxides and organic material was repeatedly extracted with ether. On evaporation a brown solid was obtained which on washing with alcohol became nearly white. It melted at 74–83° and was identified as N,N'-dibenzyl-tetrahydro-dipyridyl by the very characteristic blue color which its alcoholic or acetone solutions acquired when warmed in air.[7]

## Summary

1. Vanadous chloride reduces triphenylpyrylium chloride, forming a colored substance insoluble in water that behaves like a free radical. The same reagent reduces phenylxanthylium chloride to the free radical, phenylxanthyl, previously prepared by Gomberg.
2. Triphenylcarbinol in concd. hydrochloric acid or sulfuric acid solution is reduced to triphenylmethyl by vanadous chloride.
3. Xanthenol in concd. hydrochloric acid is reduced by vanadous chloride to bixanthyl. The color of the product indicates that a free radical is first formed which is stable only in the solid state. Benzylpyridinium chloride is reduced to a bimolecular product; no insoluble compound is formed in contrast to the behavior of the oxonium and carbonium chlorides.

Cambridge 38, Massachusetts

---

# NEW BOOKS

**The Theory of Allotropy.** By A. Smits, Ph.D., Professor of Chemistry in the University of Amsterdam. Translated from the German with the Author's sanction by J. Smeath Thomas, D.Sc., Senior Lecturer on Chemistry in the University of Liverpool. (Text-Books of Physical Chemistry, edited by Sir William Ramsay and F. G. Donnan.) Longmans, Green and Company, 55 Fifth Avenue, New York; London, Toronto, Bombay, Calcutta and Madras; 1922. xiii + 397 pp. 239 figs. 22 × 14 cm. Price $7.00 net.

Many of the writers of scientific papers published in the Netherlands seem tacitly to assume that the reader is thoroughly familiar with the writer's previous papers and can therefore without explanation apprehend the precise meaning of terms and symbols. In a series of papers this may be unavoidable, but a book made from them should surely include a fundamental discussion comprehensible to the reader not already a specialist in the topic. American readers of this book will find the explanatory matter inadequate, and the general mode of treatment is not attractive enough to persuade many of them to proceed far with the task of reading