hydrazone in ethanol are at 330-334 mμ, ε = 19,800, and at 244-246 mμ, ε = 10,300.

Anal. Calcd. for $C_8H_5N_4O_4F_3$: C, 34.53; H, 1.80; N, 20.15; F, 20.5. Found: C, 35.01; H, 1.80; N, 20.20; F, 19.14.

Trifluoroacetaldehyde *p*-Nitrophenylhydrazone.—The aqueous extract from Fraction 1 (3.5-g. aliquot) was heated with *p*-nitrophenylhydrazine (2.0 g.) in 6 *N* sulfuric acid (200 ml.). The derivative formed very slowly in low yields. Recrystallization of the red-brown solid from alcohol-water gave the *p*-nitrophenylhydrazone (0.4 g.), yellow crystals, m. p. 202-204°, dec. Absorption maxima of the hydrazone in alcohol are at 348-352 mμ, ε = 23,600, and at 236-238 mμ, ε = 8,500.

Anal. Calcd. for $C_8H_6N_3O_2F_3$: C, 41.20; H, 2.58; N, 18.03; F, 24.46. Found: C, 41.52; H, 2.69; N, 18.32; F, 23.10.

1,1,1-Trifluoro-3-nitropropane.—Rectification of Fraction 2, after removal of fluoral hydrate, yielded 1,1,1-trifluoro-3-nitropropane, b. p. 134.0-134.8° at 748 mm., n^{20}_D 1.3558, d^{20}_4 1.4220, MR_D (found) 21.72, MR_D (calcd.) 21.68. Tests for the presence of a carbonyl group in the product with neutral or acidic 2,4-dinitrophenylhydrazine were negative, but evidence for a primary nitro group was obtained when the product dissolved in 10% sodium hydroxide and then gave a nitrolic acid test when treated with potassium nitrite and hydrochloric acid.

Anal. Calcd. for $C_3H_4NO_2F_3$: C, 25.13; H, 2.80; N, 9.77. Found: C, 25.59; H, 3.15; N, 9.67.

3,3,3-Trifluoropropionaldehyde 2,4-Dinitrophenylhydrazone.—1,1,1-Trifluoro-3-nitropropane (1 g., 0.007 mole), dissolved in excess sodium hydroxide, was added, dropwise, with rapid stirring to a cold solution of 2,4-dinitrophenylhydrazine (2 g., 0.01 mole) in sulfuric acid (6 *N*, 200 ml.). (It was observed that an alkaline solution of the trifluoronitroalkane, unless kept cold, is degraded rapidly with considerable evolution of heat.) After the addition was completed, the orange precipitate was filtered, washed with sulfuric acid (6 *N*) and water, dissolved in boiling petroleum ether, and filtered to remove unreacted 2,4 - dinitrophenylhydrazine. The solution, when cooled, yielded a yellow powder which after two recrystallizations from an ethyl alcohol-water mixture, treatment with activated carbon, and two recrystallizations from a mixture of benzene and methylcyclohexane gave the 2,4-dinitrophenylhydrazone of 3,3,3-trifluoropropionaldehyde (0.4 g., 0.00137 mole, 19.6%), needles, m. p. 149.6-150.2°. A melting point of a mixture of the hydrazone with an authentic sample,[5] m. p. 150.2-150.8°, gave no depression. The principal absorption maximum of the hydrazone in alcohol is at 348-352 mμ, ε = 17,500.

Anal. Calcd. for $C_9H_7N_4O_4F_3$: C, 36.97; H, 2.38; N, 19.17. Found: C, 37.46; H, 2.28; N, 19.07.

Summary

The nitration of 1,1,1-trifluoropropane with nitric acid in the presence of oxygen at 437–462° yields 1,1,1-trifluoro-3-nitropropane (16%) and trifluoroacetaldehyde (20–24%). The specificity of the nitration reaction is attributed to the inductive effect of the trifluoromethyl group.

Trifluoroacetaldehyde resembles chloral in many of its properties. It forms a stable hydrate, undergoes a typical haloform reaction, and polymerizes during storage. The polymerization is reversed by heat or dilute bases.

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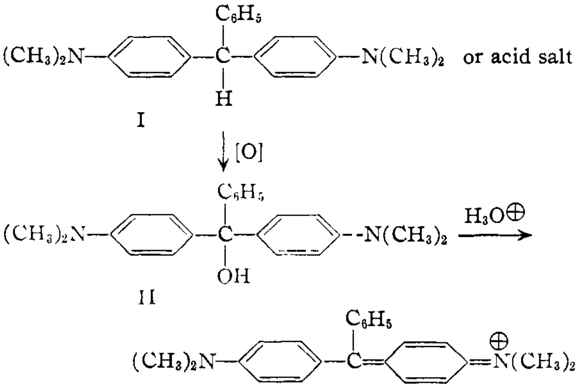
[CONTRIBUTION NO. 1174 FROM THE GATES AND CRELLIN LABORATORIES, CALIFORNIA INSTITUTE OF TECHNOLOGY, AND THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Mechanism of Oxidation of Leuco Malachite Green by Ceric Sulfate[1]

BY C. GARDNER SWAIN AND KENNETH HEDBERG

The mechanism of oxidation of carbon-hydrogen bonds in acid solution by oxidizing agents of high electrochemical potential such as potassium permanganate, ceric sulfate or lead dioxide has never been satisfactorily settled. It is customary to write successive replacements of hydrogen by hydroxyl, splitting out water where possible. For example, the oxidation of leuco malachite green (I) to malachite green (III) by any of these oxidizing agents in acid solution has generally been regarded as yielding first the carbinol or colorless "color base" (II) as the primary oxidation product, which is subsequently dehydrated to the dye (III).[2] Similarly, $CH_3CH(OH)_2$ is frequently considered as an intermediate in the oxidation of ethanol to acetaldehyde.[3] These hydroxylations have been suggested as merely convenient ways of thinking, enabling one to predict the products obtained; there has been no evidence either supporting or disproving them as actual mechanisms.



The present study proves that carbinol (II) is *not* an intermediate in the conversion of leuco malachite green to dye in aqueous acid solution at room temperature when ceric sulfate is used as the oxidizing agent. The proof rests on the

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(1) Paper presented at 113th Meeting, American Chemical Society, Chicago, Illinois, April 20, 1948.

(2) Conant and Blatt, "Chemistry of Organic Compounds," third ed., Macmillan Company, New York, N. Y., 1947, pp. 532–533; Conant, *ibid.*, first ed., 1933, pp. 504–505.

(3) Fieser and Fieser, "Organic Chemistry," D. C. Heath and Company, Boston, Mass., 1944, pp. 130–131.

observation that carbinol is dehydrated to dye more slowly than leuco base is oxidized to dye under comparable conditions. The curves shown for leuco base, carbinol base, and dye in Fig. 1 (for *p*H 3.0) and Fig. 2 (for *p*H 3.6) converge and are indistinguishable after several hours. The final solutions contain, in addition to dye, a considerable concentration of carbinol in equilibrium with the dye, due to the acidity and the high ionic strength employed.[4] This explains why the dye fades and why the curves for carbinol simply approach the equilibrium color asymptotically, while the curves for leuco base have maxima. Since the leuco base does not give dye *via* the carbinol base, the latter must subsequently form from the dye. In Fig. 1 the maximum dye concentration is attained in about ten minutes. The curve for leuco base to the right of this maximum is almost exactly superimposed on the curve for dye by shifting it ten minutes to the left.

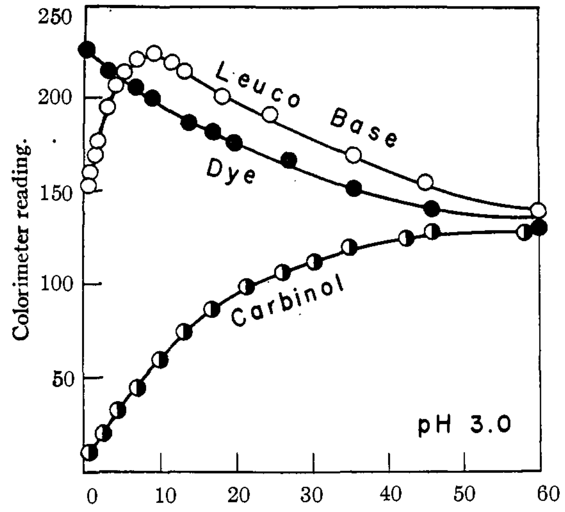
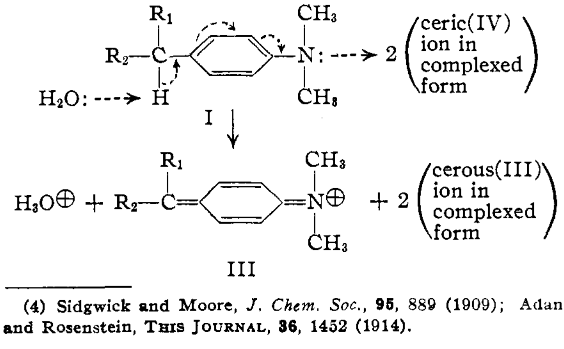


Fig. 1.—Experiments at *p*H 3.0 ± 0.03: ○, 9.1 × 10^{-5} *M* leuco malachite green, 1.82 × 10^{-4} *M* ceric ion; ◑, 9.1 × 10^{-5} *M* carbinol, 1.82 × 10^{-4} *M* cerous ion; ●, 9.1 × 10^{-5} *M* malachite green, 1.82 × 10^{-4} *M* cerous ion.



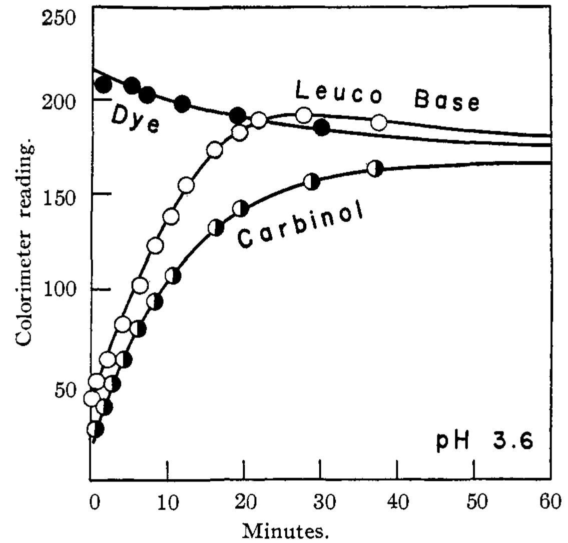


Fig. 2.—Experiments at *p*H 3.6 ± 0.03: ○, 9.1 × 10^{-5} *M* leuco malachite green, 1.82 × 10^{-4} *M* ceric ion; ◑, 9.1 × 10^{-5} *M* carbinol, 9.1 × 10^{-5} *M* ceric ion; ●, 9.1 × 10^{-5} *M* malachite green, 9.1 × 10^{-5} *M* ceric ion.

A mechanism is suggested involving a nucleophilic attack by a water molecule on the central hydrogen atom, concerted with electron-removal from the nitrogen atom by the oxidizing agent. Valence states of IV, III and 0 are the only ones known for cerium. The equation may represent two electrons being transferred simultaneously to two ceric ions; or one electron may first be removed from nitrogen by one ceric ion, followed by concerted attack of water and the second ceric ion on the semi-oxidized amine cation.

There are two phases in the oxidation of leuco base. A part of the leuco base is oxidized within a few seconds by the ceric salt, and the rest only slowly. The appearance of color in the rapid phase (*e. g.*, the rise from 0 to 150 in Fig. 1) could be easily followed by the eye, but was too rapid for our colorimetric measurements. The fraction which is oxidized very rapidly increases with increasing acidity. The same phenomenon is observed in the oxidation of iodide ion by ceric sulfate in the presence of starch as indicator (see Fig. 3). This behavior may thus be attributed to some characteristic of the oxidizing agent, rather than of the leuco malachite green.

Since potassium permanganate and lead dioxide in acid solution are oxidizing agents of high potential, exhibiting much the same reactivity toward different classes of organic compounds as ceric sulfate, it seems probable that they also would oxidize leuco malachite green directly to the dye. Indeed, rough experiments show that potassium permanganate oxidizes leuco malachite green at a rate comparable to the ceric sulfate oxidation under similar conditions. Furthermore, because the electronic situation is so closely analogous, it seems probable that oxidation of alcohol by these agents also does not involve intermediate hydroxylation of the carbinol carbon, but instead involves only attack of water on

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[4] Sidgwick and Moore, *J. Chem. Soc.*, **95**, 889 (1909); Adams and Rosenstein, THIS JOURNAL, **36**, 1452 (1914).

the hydrogen on this carbon, concerted with some type of electron-removal from the oxygen atom by the oxidizing agent.

Experimental

Reagents.—Two samples of leuco base were used. The first sample was the lowest melting allotrope; its m. p. 92-93°, compares well with the m. p. previously reported.[5] It was obtained by recrystallizing 5 g. of a crude product twice from 50 cc. of 95% ethanol, once from a benzene-ethanol mixture, and finally from ligroin, and drying. Solutions (0.001 *M* in 0.01 *M* sulfuric acid) less than one day old were satisfactory, but aged solutions of this sample gave only a small fraction of the expected color in acid ceric sulfate solutions. The second sample was an Eastman Kodak Co. product, No. 3620, white crystals, m. p. 102-102.5°. Solutions of this material were stable in air indefinitely, whether the sample was recrystallized first or not.

Two solutions of malachite green dye also gave similar kinetic results. The first of these was prepared directly from National Aniline certified grade malachite green oxalate. The second was made from the same source material but involved first the preparation of the carbinol. Six grams was dissolved in 600 cc. of distilled water and the carbinol precipitated by adding 60 cc. of 1 *M* sodium hydroxide. This was filtered off and recrystallized twice from 95% ethanol containing a trace of dissolved potassium hydroxide. It was then washed with ether and finally crystallized from ligroin. After drying, the resulting white material had a melting point of 121-121.5°, which compares well with the value of 120-122° previously reported for the higher melting allotrope.[6] An acid solution of this (2×10^{-5} *M* in 6×10^{-5} *M* sulfuric acid) rapidly reverted to dye.

Ceric bisulfate, $Ce(HSO_4)_4$, C. P. anhydrous G. F. Smith material, and reagent grade ammonium sulfate, cerous nitrate hexahydrate and sulfuric acid were used.

Procedure.—All reaction mixtures contained an ammonium sulfate-bisulfate buffer and were adjusted to constant high ionic strength ($^1/_2 \sum c_i z_i^2 = 2.4 \pm 0.1\ M$). The *p*H values were measured with a glass electrode and have an uncertainty of ± 0.03 unit. The rate of formation of malachite green dye was measured with a Klett-Summerson photoelectric colorimeter and a red filter. In a Klett tube of about 15-cc. capacity was placed 1.0 cc. of 0.001 *M* leuco base in 0.01 *M* sulfuric acid. The oxidizing solution, consisting of 2.0 cc. of 0.001 *M* ceric tetrabisulfate in 0.02 *M* sulfuric acid, 2.7 cc. of 3.29 *M* ammonium sulfate and 6.3 cc. of distilled water (or sulfuric acid or sodium hydroxide as desired to vary the *p*H), was made up in a separate tube immediately before use. Solutions were kept in a water-bath at 24.0 ± 0.1° whenever colorimeter readings were not actually being taken. At zero time the oxidizing mixture was poured into the leuco dye; the resulting solution was shaken, placed in the colorimeter, and the measurements begun. Duplicate experiments were carried out with carbinol and with dye, substituting cerous ion for ceric ion. In the case of carbinol the procedure had to be slightly modified. The cerous solution (2.0 cc. of 0.001 *M* cerous nitrate in 0.02 *M* sulfuric acid) was placed in the Klett tube together with 0.2 cc. of 0.1 *N* sulfuric acid and 2.7 cc. of ammonium sulfate solution. In the other tube was placed 1.0 cc. of 0.001 *M* malachite green dye, 0.2 cc. of 0.1 *N* sodium hydroxide and 5.9 cc. of distilled water. About forty-five minutes were allowed for formation of the carbinol before mixing the solutions. At the end of this time the dye solution had become colorless. It was sometimes turbid due to insolubility of the carbinol, but addition of the acid salt solution always clarified it immediately. Ceric ion rather than cerous ion was present with carbinol and dye in the runs at *p*H 3.6, but it was found that within experimental error this substitution did not affect the reading of the colorimeter. All runs were done at 24 ± 0.1°. The ceric and cerous solutions were always clear to the eye over the range of *p*H studied.

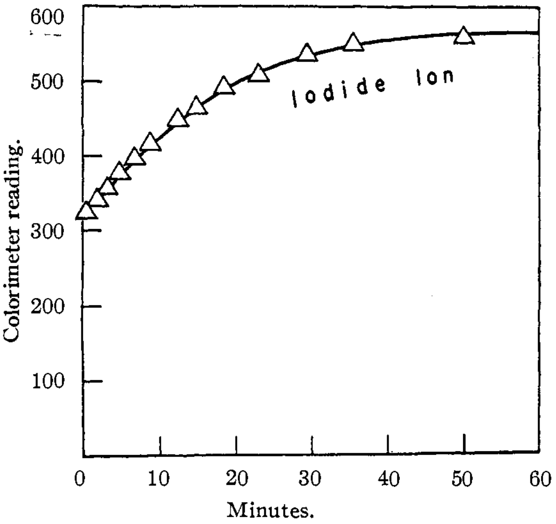

Fig. 3.—Oxidation of excess iodide ion by 9.1×10^{-5} *M* ceric ion at *p*H 3.0 in the presence of starch indicator.

The rate of dehydration of carbinol to dye was found to pass through a minimum between *p*H 3 and 4. A 25° and 2.8 *M* ionic strength (slightly different conditions than used above), the first order rate constants at *p*H 2.98, 4.08 and 4.69, are 8.9, 6.6 and 13.5 × 10^{-4} sec.$^{-1}$, respectively. Near the minimum the carbinol solution probably exists to the maximum extent in the form of its diprotonated conjugate acid. The more acid or basic forms might be expected to be more reactive from a consideration of electrical effects.

Summary

It is commonly assumed that the carbinol base is an intermediate in the oxidation of leuco malachite green to malachite green dye, which proceeds extremely rapidly with acid solutions of ceric sulfate, potassium permanganate, or lead dioxide. It is interesting to study this oxidation, since it serves as a convenient model for the oxidation of carbon–hydrogen bonds in many other systems.

This work proves that the carbinol is not an intermediate in the oxidation with ceric sulfate, since it is dehydrated to dye more slowly than the leuco base is oxidized to dye under comparable experimental conditions.

A mechanism is suggested which is consistent with the known facts.

CAMBRIDGE, MASS. RECEIVED JANUARY 4, 1950

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[5] E. Fischer, O. Fischer and O. Lehmann, *Ber.*, **12**, 798 (1879).

[6] Villiger and Kopetschni, *ibid.*, **45**, 2916 (1912).