Reversible Oxidation of Guanidinium Ion

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Some years ago the senior author and Dr. D. F. Herman[3] attempted a synthesis of 2-aminopyrimidine by condensing guanidine and glycerol in concentrated sulfuric acid solution containing any one of a variety of oxidants.[4] The one reaction mixture from which the desired compound was isolated in poor yield contained potassium persulfate. In that mixture a transient blue color appeared in the early heating stages of the reaction. This paper concerns itself with the nature of that blue intermediate.

Elimination experiments showed that the blue color was due to the oxidation of guanidinium (guanidinous) ion by persulfate ion. 90% Aqueous hydrogen peroxide was an effective susbtitute for potassium persulfate, but no replacement was found for the solvent. Among the many solvents tried were glacial acetic acid, methanesulfonic acid, ethanesulfonic acid, and 20% fuming sulfuric acid. In view of the ineffectiveness of the last solvent it seems that permonosulfuric (Caro's) acid rather than perdisulfuric acid was the active oxidant. Treatment of the blue sulfuric acid solutions with zinc, tin, or hydrogen sulfide resulted in bleaching. The full intensity of color returned on retreatment with an excess of either of the effective oxidants.

Spectrophotometric measurements showed that Beer's law was obeyed at both 613 mμ and 650 mμ on dilution with either concentrated or 20% fuming sulfuric acid. The absorption spectra of solutions made from varying ratios of persulfate to guanidinous ions (0.2/1 to 3.7/1 milliequivalents) were identical, as shown in Fig. 1. These results demonstrated the presence of a single absorbing species.

The stoichiometry of the reaction was studied by measuring the transmission at 650 mμ at room temperature as a function of persulfate concentration at fixed concentrations of the reductant. These experiments were complicated by the slow rate of oxidation of guanidinous ion. This permitted a considerable loss of oxidant by autodecom-
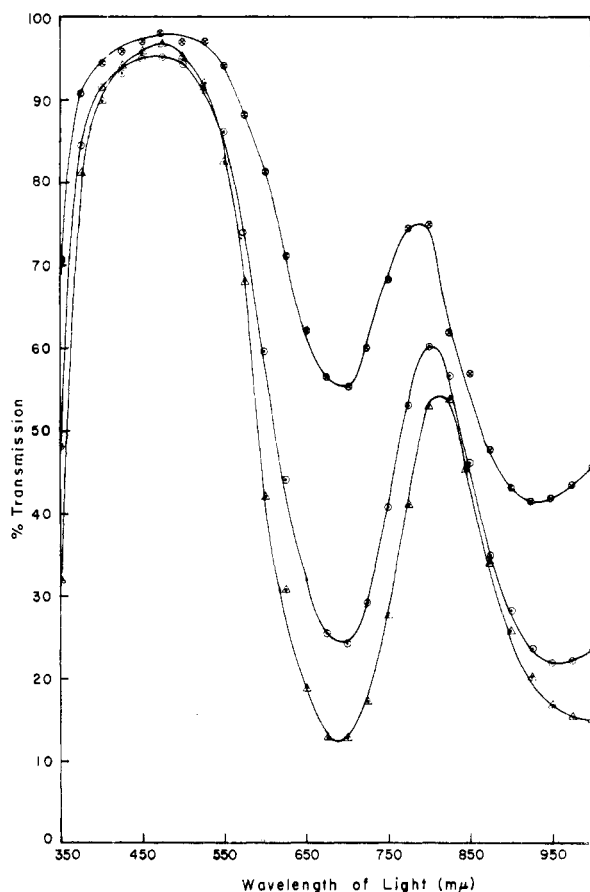

Fig. 1. Absorption spectrum of guanidinic sulfate in sulfuric acid. ⊗ 0.194 milliequivalents of $K_2S_2O_8$ to 5 ml. of 0.185 molar guanidinous sulfate in sulfuric acid. ⊙ 0.744 milliequivalents of $K_2S_2O_8$ to the same volume of reductant solution. △ 2.56 milliequivalents of $K_2S_2O_8$ to the same volume of reductant solution

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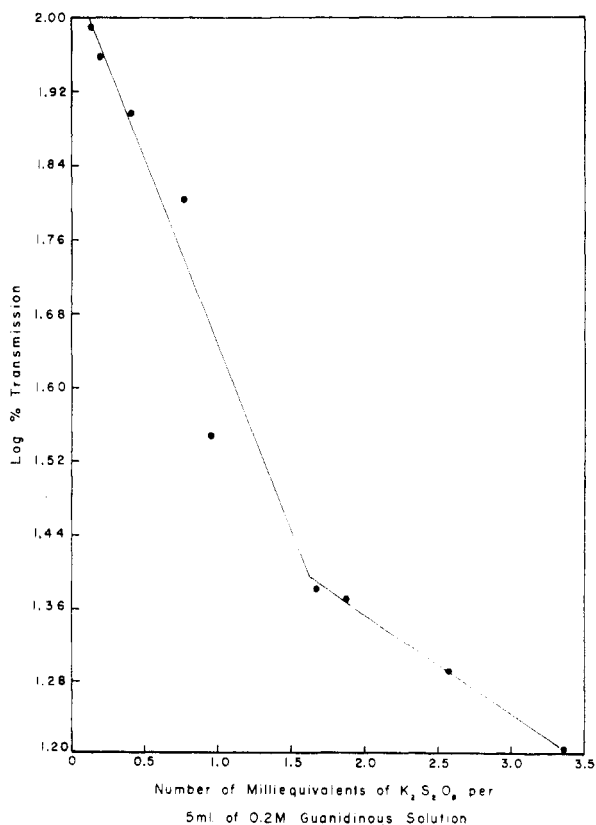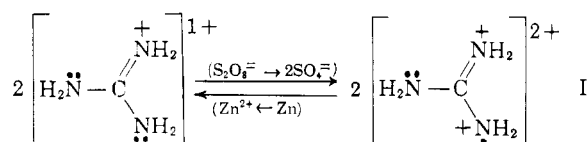(4) Unpublished experiments.

Fig. 2. Extent of oxidation of guanidinous to guanidinic ions by persulfate ion in sulfuric acid

position before equilibrium was established. For a 0.2 molar guanidinous solution a break in the absorption curve occurred at a ratio of about 1.6/1 milliequivalents of oxidant/reductant (assumption of one equivalent per mole of reductant) as shown in Fig. 2.

None of the attempts to correct for the autodecomposition of the oxidant proved satisfactory. The addition of an excess of a standard reductant to the concentrated sulfuric acid solution followed by its back titration proved to be an inaccurate measure of total remaining oxidant because the solvent itself contributed to the oxidant capacity. Dilution of the reaction mixture with ice or iced sodium bicarbonate solutions before so measuring total oxidant also gave erratic results. Measurements of the rate of oxygen evolution in a Warburg apparatus offered some promise. However, the rate was complicated by its dependence on product as well as reactant concentrations. In any case, the fact that the break in Figure 2 occurred at an equivalent ratio significantly less than 2/1, coupled with the finding of a single light absorbing species strongly suggests that the oxidation equivalent of guanidinous ion is one electron/mole.

The stability of guanidinic ion in sulfuric acid is understandable in terms of resonance theory. The existence of three symmetrical resonance forms of guanidinous ion "explains" the basic strength of guanidine. In the case of guanidinic ion (I) there are six such forms together with others which make smaller contributions to the state of the ion. The bracketed ions shown below are single resonance forms in which the unbounded electrons and charges have been localized.

$$2\left[\mathrm{H_2\ddot{N}-C}\begin{matrix}\overset{+}{N}H_2\\ \\ \ddot{N}H_2\end{matrix}\right]^{1+} \underset{(Zn^{2+}\leftarrow Zn)}{\overset{(S_2O_8^= \rightarrow 2SO_4^=)}{\rightleftarrows}} 2\left[\mathrm{H_2\ddot{N}-C}\begin{matrix}\overset{+}{N}H_2\\ \\ +\dot{N}H_2\end{matrix}\right]^{2+} \quad \mathrm{I}$$

It is only in such a powerful proton donor as concentrated sulfuric acid that the doubly positive

ated dimer by condensing cyanamide and hydrazine. It was assumed that if any of the free base were formed, it would dissociate to yield guanidinic ion. No blue color was observed on solution of the reaction mixture in sulfuric acid.

Many attempts to crystallize guanidinic sulfate by cooling its solution with and without the addition of other solvents failed. The addition of water, methanol, acetic acid, or diethyl ether caused immediate bleaching even at $-10°$. Dilution with ether and Dry Ice at $-80°$ resulted in color retention, but fading set in as the solution warmed up. No color remained at $-25°$.
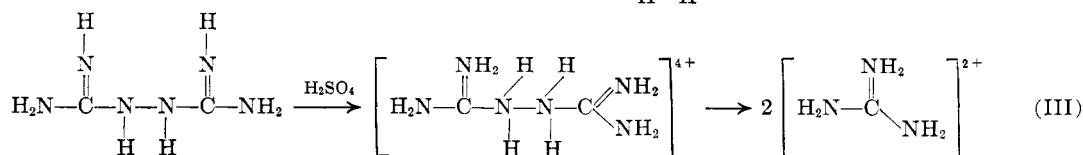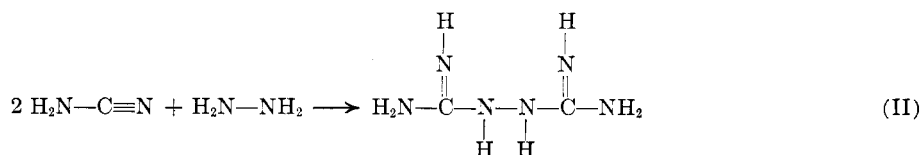
The dilution of the guanidinic sulfate solution with a variety of liquids led to observations of some analytical interest.

1. Dilution with water produced a gas which oxidized iodide ion (potassium iodide paper). The diluted solution contained no guanidinous ion. If a guanidinic solution was first reduced with tin before dilution, guanidinous ion was readily detected.[5]

2. Aromatic hydrocarbons and their chlorinated derivatives may be distinguished from alkanes and their chlorinated derivatives. The former group in contrast to the latter reduced guanidinic sulfate, causing a color change from blue to green, orange, or brown.

These experiments were done with guanidinic sulfate solutions which were at least a month old so as to insure the complete absence of permonosulfuric acid. It was established[6] that the latter was but slightly detectable after one week and absent after two weeks at room temperature in concentrated sulfuric acid.

Several derivatives of guanidine were oxidized by permonosulfuric acid in sulfuric acid solution to yield deep red-brown solutions. These were: phenylguanidine carbonate, diphenylguanidine, triphenylguanidine, phenylbiguanide hydrochloride, and o-tolylbiguanide hydrochloride. In view of the fact that the common amides and ureas give no such colors on contacts with this reagent, these observations constitute a qualitative test for the guanidine group.

$$2\ \mathrm{H_2N-C\equiv N + H_2N-NH_2 \longrightarrow H_2N-\overset{\overset{\displaystyle H}{|}\overset{\displaystyle N}{\|}}{C}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{N}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{N}}-\overset{\overset{\displaystyle N}{\|}}{\underset{}{C}}-NH_2} \qquad \mathrm{(II)}$$

$$\mathrm{H_2N-\overset{\overset{H}{|}\overset{N}{\|}}{C}-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{N}}-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{N}}-\overset{\overset{N}{\|}}{C}-NH_2} \xrightarrow{\mathrm{H_2SO_4}} \left[\mathrm{H_2N-\overset{\overset{NH_2}{\|}}{C}-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{N}}-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{N}}-C\overset{NH_2}{\underset{NH_2}{\diagup}}}\right]^{4+} \longrightarrow 2\left[\mathrm{H_2N-\overset{\overset{NH_2}{\|}}{C}\underset{NH_2}{\diagdown}}\right]^{2+} \quad \mathrm{(III)}$$

guanidinic ion could exist. Although it seemed improbable that guanidinic ion would dimerize, hydrazine was sought in solutions which were diluted and hydrolyzed. It could not be detected. An attempt was also made to synthesize the unproton-

(5) Bulletin on sodium β-naphthoquinone-4-sulfonate, Eastman Kodak reagent #1372, Eastman Kodak Co., Rochester, N. Y.

(6) S. Soloway and A. Santoro, Anal. Chem., 27, 798 (1955).

Preparation of guanidinic sulfate and test of Beer's law. Eighteen grams (0.1 mole) guanidine carbonate, purified by recrystallization from water, was dissolved in 100 ml. of ice cold concentrated sulfuric acid. To this solution was added another composed of 27 g. (0.1 mole) potassium persulfate dissolved in 100 ml. of concentrated sulfuric acid. The resulting solution was allowed to warm up to room temperature and stand overnight for full color development. Aliquots were then diluted proportionately with concentrated and 20% fuming sulfuric acids. The per cent transmission at 613 mμ and 650 mμ was determined with a Beckmann DU Spectrophotometer.

Reversibility of the redox system. Aliquots of the above guanidinic sulfate solution were treated with tin, zinc, and anhydrous hydrogen sulfide until almost visually colorless. A brown-pink tint remained in the reduced solutions. The solutions were then reoxidized with excess solid potassium persulfate. The original solution transmitted 3.5% of the incident red light, the reduced solution 96%, and the reduced and reoxidized solution 2%. These measurements were made with a Leitz photoelectric colormeter using filter f-244.

Absorption spectra. To 5 ml. aliquots of a 0.185 molar guanidinous solution were added solid potassium persulfate in amounts equal to 0.103, 0.194, 0.382, 0.744, 0.937, 1.67, 1.85, 2.56, and 3.34 milliequivalents. The per cent transmission of these solutions at various wave lengths was measured with the Beckmann spectrophotometer. For the sake of clarity only three of the family of nine curves are shown in Fig. 1.

Stoichiometry. Weighed quantities of potassium persulfate were added to 5 ml. aliquot of 0.185 molar guanidinous solution. The percent transmission at 650 mμ was again determined with the Beckmann spectrophotometer.

Analytical test for guanidine and derivatives. About 10 mg. of substance were dissolved in 2 ml. of concentrated sulfuric acid. To the resulting solution was added about 30 to 40 mg. of potassium persulfate. On warming or standing at room temperature a blue or deep red-brown color developed.

Test for persulfate and permonosulfate ions.[6] This was identical with the test for phenols with free para positions in which the diluted and neutralized solutions of the above ions were used as the source of oxidant.

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On the Oxidation of Desoxybenzoins

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It has been shown[1] by A. Robertson *et al.*, that some desoxybenzoins can be oxidized by potassium permanganate to the corresponding benzoins. Further, it was found by these and other authors that oxidation of some derivatives of flavanone,[2]

(1) (a) G. G. Badcock, G. W. K. Cavill, A. Robertson, and W. B. Whalley, *J. Chem. Soc.*, 2961 (1950). (b) After the present work had been completed, the writer received the July 1957 copy of *J. Chem. Soc.* in which Robertson *et al.* showed that the oxidation product of desoxybenzoins was a benzil and not a benzoin as they had previously considered.

(2) A. Robertson and W. B. Whalley, *J. Chem. Soc.*, 1440 (1954).

isoflavanone,[3] and coumaranone[4] by permanganate produced compounds having a hydroxyl group alpha to the carbonyl group.

In the course of investigation[5] on the coloring matter of *Sophora japonica*, *L.*, potassium permanganate oxidation of 2-hydroxy-2',4',4'-trimethoxydesoxybenzoin (I, R = OCH₃, R' = OH, R'' = H) in refluxing anhydrous acetone produced a compound $C_{34}H_{34}O_{10}$, melting at 226–227°, in a moderate yield. It has now been confirmed that this compound is a bisdesoxybenzoin derivative having the formula (II, R = OCH₃, R' = OH).
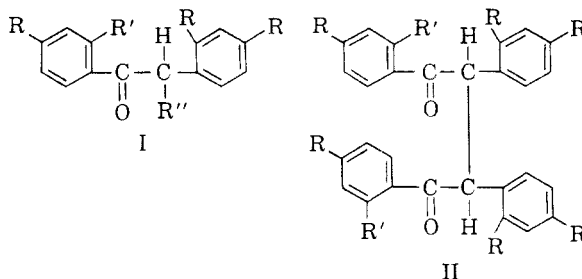
The ultraviolet absorption spectrum (Figure 1, curve c) of this compound showed almost the same shape as that of the parent desoxybenzoin. The
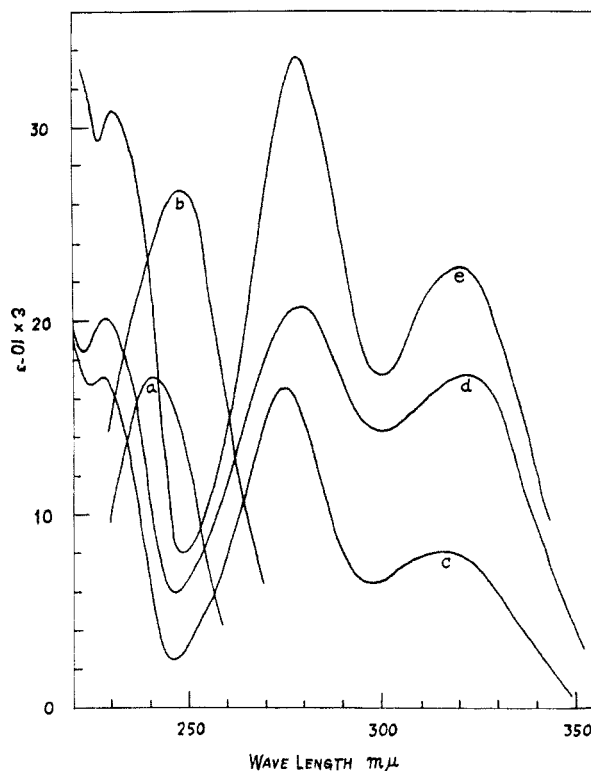

Fig. 1. Ultraviolet absorption spectra: a, Desoxybenzoin; b, Bisdesoxybenzoin; c, 2-hydroxy-2',4,4'-trimethoxydesoxybenzoin; d, 2-hydroxy-2',4,4'-trimethoxybenzil; e, Bis-2-hydroxy-2',4,4'-trimethoxydesoxybenzoin

(3) V. B. Mahesh and T. R. Seshadri, *J. Chem. Soc.*, 2503 (1955).

(4) J. Gripenberg, *Acta Chem. Scand.*, 7, 1323 (1953).

(5) Unpublished paper.