were obtained by concentrating the mother liquors and recrystallizing; yield, 0.0578 g. The product is sparingly soluble in cold water and dilute hydrochloric acid, readily soluble in alcohol and in ether.

Anal. Calcd. for $C_{12}H_{20}O_2N_2S_2$: N, 9.72; S, 22.22. Found: N, 9.53; S, 22.36.

The same product was obtained by aeration: to a solution of 0.2 g. of the ethiodide in 10 cc. of water, 2 *N* sodium hydroxide was added until the *p*H was 10. A trace of ferrous sulfate was added and air was bubbled through the solution for forty hours. A yield of 0.072 g. of colorless needles, m. p. 101–102°, separated during the aeration; further quantities were obtained by extraction with ether.

2,4-Dimethyl-3-phenylthiazolium Salts.—A mixture of 7.0 g. of thioacetanilide, 5.7 g. of chloroacetone, and 5 cc. of absolute alcohol was boiled gently under reflux for one and one-half hours and then evaporated at 100°. The sirupy residue was repeatedly stirred with ether; the insoluble portion was dissolved in water and decolorized with charcoal. The chloride could not be crystallized; addition of picric acid caused the precipitation of an oil. Platinic chloride yielded a crystalline platinichloride, insoluble in water and in alcohol, which melted with decomposition at 245° after darkening at 240°.

Anal. Calcd. for $C_{22}H_{24}N_2S_2Cl_6Pt$: C, 33.49; H, 3.05; S, 8.13; Pt, 24.77. Found: C, 33.50; H, 2.80; S, 8.35; Pt, 24.86.

On adding potassium iodide in excess to an aqueous solution of the chloride, the iodide crystallized in the form of colorless needles, soluble in water, ethyl alcohol, chloroform, and ethylene chloride, sparingly soluble in butyl alcohol, insoluble in acetone, m. p. 210°.

Anal. Calcd. for $C_{11}H_{12}NSI$: C, 41.77; H, 3.79; N, 4.42; S, 10.09; I, 40.1. Found: C, 41.73; H, 3.49; N, 4.47; S, 10.19; I, 39.76.

No sulfate is formed by the action of bromine upon this substance, either in the cold or on warming for a short time. With alkaline plumbite, lead sulfide is rapidly produced at 95°.

4-Methyl-3-phenylthiazolium Iodide.—A mixture of 2.0 g. of thioformanilide and 5 cc. of chloroacetone was warmed to 50° for a few minutes; the resulting solution was allowed to cool to room temperature during two hours. On addition of ether, the product precipitated as a liquid. This was dissolved in 50 cc. of water, decolorized with charcoal, and treated with 3 g. of potassium iodide. The crystals which formed were recrystallized from water: colorless, rectangular plates, m. p. 241°.

Anal. Calcd. for $C_{10}H_{10}NSI$: S, 10.56; I, 41.9. Found: S, 10.67; I, 41.9.

The properties of this iodide closely resemble those of the 2,4-dimethyl compound.

Summary

1. The acid $C_5H_5O_2NS$ obtained by Windaus and collaborators by the action of nitric acid upon vitamin B_1 is shown to be 4-methylthiazole-5-carboxylic acid.

2. The basic product, obtained by Williams and his colleagues by treating vitamin B_1 with sulfite, is shown to be 4-methyl-5-β-hydroxyethylthiazole. This substance has been synthesized.

3. Experimental evidence is given in support of the view that the thiazole exists in the vitamin in the form of a quaternary salt.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

The Action of Hydrogen Bromide on the Nitrogen Afterglow

BY W. H. RODEBUSH AND M. L. SPEALMAN

Rodebush and Ewart[1] reported that the addition of hydrogen bromide to the nitrogen afterglow, produced in moist nitrogen by means of the electrodeless discharge, caused quenching of the nitrogen afterglow with the simultaneous production of a brilliant orange glow at the point where the gases mixed. When this orange light was viewed with a small spectroscope, it appeared to consist of the prominent red and yellow first positive bands of nitrogen, and an orange band which they also attributed to nitrogen. With hydrogen iodide they observed that the nitrogen afterglow was quenched, and that a blue afterglow was produced which extended from the point where the gases mixed to the liquid-air cooled trap of the mercury vapor diffusion pump. This blue afterglow was attributed to iodine. With both hydrogen bromide and hydrogen iodide, considerable quantities of the corresponding ammonium halide were produced in the reaction tube.

It has been suggested, however, that the orange bands might be bromine bands. If this were true, the reactions of hydrogen bromide and hydrogen iodide with active nitrogen would be entirely similar since there was no doubt that the spectrum obtained when hydrogen iodide is added to active nitrogen is due to the iodine molecule. The behavior in the two cases, however, is so different as to cast doubt upon this point of view. The

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[1] Ewart and Rodebush, THIS JOURNAL, **56**, 97 (1934).

luminescence of the hydrogen bromide is emitted in the immediate vicinity of the point of mixing, no matter how rapid the flow of gases. The primary reaction is presumably

$$N + HBr = NH + Br$$

Bromine molecules would therefore have to be formed by a following reaction which must be slow, and the concentration of bromine molecules must therefore be very low at the point of admission of the hydrogen bromide. It is possible for a bromine molecule to be formed by direct combination of an excited and unexcited bromine atom, but the probability of this process is extremely small.[2] A spectrographic investigation was the obvious solution to this question. The only difficulty is that, on account of the low intensities, it is not possible to use a very high dispersion.

Experimental

The electrical apparatus used with the electrodeless discharge was identical with that used in the work mentioned previously. A flowing system was used in which nitrogen was pumped through a Pyrex glass tube having a length of a meter or more, and an internal diameter of about 2.5 cm. The exciting coil was wrapped around this tube at the inlet end. The light from the discharge was prevented from reaching the slit of the spectrograph by surrounding the discharge region with a box, and by means of two right angle bends in the glass tube. The photographs were taken end-on of a 25-cm. section of the tube through either quartz or Pyrex glass windows. The connection to the vacuum pumps was about 3 cm. from the window. At the other end of this 25-cm. section of the tube the gas to be added to the nitrogen afterglow was introduced. A right angle bend in the reaction tube at this point served to prevent quite completely the superposition of the nitrogen afterglow spectrum on the photographic plate when something else was being photographed.

Fig. 1.

The upper photograph in Fig. 1 is a four-hour exposure of the nitrogen afterglow; the lower photograph is a two-hour exposure of the light produced on adding hydrogen bromide to the nitrogen afterglow. These pictures were taken consecutively on the same plate by using adjacent openings in the slide covering the slit of the spectrograph. Great care was taken not to jar the spectrograph or move the plate-holder during these exposures. A Hilger E-1 spectrograph having a glass optical system was used for these photographs. The slit width was about 0.05 mm.; the plate was a Type I-F Eastman spectroscopic plate.

Since the two exposures are of unequal length, no comparison of intensities may be made between them. The important point is that no bands appear in one exposure which are not present in the other. Under a low dispersion the first positive (afterglow) bands of nitrogen appear to have four or five heads. The effect of the presence of the hydrogen bromide is greatly to intensify two of these heads in certain bands while certain other bands as a whole are greatly weakened. The following tabulation of results may be made.

Table I

Transition (V′ − V″)	Effect	Transition (V′ − V″)	Effect
11–6	Greatly diminished intensity	13–9	Marked increase in intensity of two heads
10–5		9–5	
9–4		8–4	
12–8		7–3	
11–7		6–2	
10–6		12–9	
		11–8	
		10–7	
		9–6	

In connection with this action of hydrogen bromide it is of interest that bromine produced the same effects as hydrogen bromide on the distribution of intensities, so far as one could tell from spectrograms taken with a Bausch and Lomb quartz spectrograph. The Bausch and Lomb instrument, however, has a much lower dispersion than the Hilger spectrograph used. However, the similarity was so marked as to leave little doubt, and it therefore seems that it is the bromine atom rather than the hydrogen bromide molecule which is responsible for the effects observed.[3]

The blue afterglow produced by adding hydrogen iodide to the nitrogen afterglow was photographed with a Bausch and Lomb quartz spectrograph, and was found to consist of a continuum extending from 4800 to 2200 Å. interspersed with a great many broad, diffuse bands. Presumably this is a fluorescence spectrum of iodine.

Summary

The relative intensity of certain transitions in the nitrogen afterglow is greatly altered by the presence of hydrogen bromide or bromine, but the band spectrum of bromine was not observed.

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[2] Urey and Bates, *Phys. Rev.*, **34**, 1541 (1929).

[3] On adding Br_2 there was considerable attack of the glass with the production of pale yellow transparent flakes. The product was not identified, but was found to be insoluble in hot and cold dilute acid and alkali.