



Their determinations of vapor pressure indicate a boiling point of -13° , which throws discredit on the boiling point given by Müller. They state that the compound is completely decomposed at 170° and assume that it decomposes to nitrogen dioxide and chlorine and that these do not combine at any temperature. The experiments recorded above do not altogether agree with this. They also indicate that nitryl chloride decomposes to nitrosyl chloride and oxygen as well as to nitrogen dioxide and chlorine.

Summary

Nitryl chloride has been prepared by the action of hydrochloric acid on nitrogen tetroxide, by the action of phosphorus pentachloride on lead nitrate, and by the union of nitrogen dioxide and chlorine.

The method of Schumacher and Sprenger by the action of ozone on nitrosyl chloride is undoubtedly better. That method, combined with the method of Whittaker, Lundstrom and Merz¹¹ for preparing nitrosyl chloride will make nitryl chloride and nitrosyl chloride easily accessible for both laboratory and commercial use.

¹¹ Whittaker, Lundstrom and Merz, *Ind. Eng. Chem.*, **23**, 1410 (1931).

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THE EFFECT OF SUPERSONIC RADIATION ON BROM THYMOL BLUE

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In 1929, Schmitt, Johnson and Olson¹ reported that various substances can be oxidized by subjecting solutions of such substances to ultrasonic vibrations under such conditions that air or oxygen can be cavitated from the solutions. In particular, experiments were conducted upon dilute aqueous solutions of brom thymol blue, without specifying how dilute those solutions were. Quoting from their article, "Subsequent tests showed that when a dilute aqueous solution of brom thymol blue (to which sufficient sodium hydroxide was added to produce a blue green color) was radiated, the solution changed to yellow in a very short time. It was easy to demonstrate that comparatively few of the dye molecules were destroyed in the process of radiation, for addition of alkali caused a prompt return of the blue color. Other indicators, such as brom phenol blue and litmus were affected in a similar manner. Whatever the process may be, there is no

¹ Schmitt, Johnson and Olson, *THIS JOURNAL*, **51**, 370 (1929).

doubt that dye molecules were altered by the radiation and gave rise to hydrogen ions." An attempt to repeat some of this work was made by Szu-chih Liu and Hsien Wu.² They confirmed the conclusion of Schmitt, Johnson and Olson, that the presence of oxygen was necessary, but stated that "the indicators are permanently destroyed under the influence of ultrasonic radiation. A change of hydrogen-ion concentration may occur as a result of this destruction, but the fading of the color is due to the destruction of the indicator and not to any change in the hydrogen-ion concentration." They based this conclusion on the observation that the indicator solution became colorless without passing through the yellow stage, and that the addition of alkali did not cause the return of the blue color.

The only point at issue between the two groups of investigators is the concentration of hydrogen ion produced, and the concentration of indicator molecules which remain after radiation, since both groups agree that some indicator molecules are destroyed. The most obvious explanation of the apparent discrepancy between the two investigations lies in the probable difference of the initial concentration of indicator and hydrogen ion. Nevertheless, the experiments have been repeated and extended as described below.

The oscillator was essentially the same as that used by Schmitt, Johnson and Olson. The brom thymol blue was identical with that used in the original investigation. It was not recrystallized or purified, but was dried at 108° for two hours; 0.25 g. was shaken with a liter of distilled water, and then decanted. This solution, which corresponds closely with that used by Schmitt, Johnson and Olson, will be called Solution A. Another liter of distilled water was poured upon the residual crystals, and after shaking and standing for some time, it was decanted. This solution will be referred to as Solution B. A third solution, C, was made by dissolving 0.081 g. of the indicator in a liter of water. This corresponds to a concentration of $1.3 \times 10^{-4} M$. The usual stock indicator solution is made by dissolving 0.04 g. of indicator in 100 cc. of 95% alcohol, which corresponds to 6×10^{-4} mole liter, and so the titration is carried out with an indicator concentration of about $3 \times 10^{-6} M$. This procedure was not followed, in order to avoid the introduction of any extraneous material. The P_H values were determined by comparing with Clark's³ color chart.

Solution A appeared to be more orange than B. The behavior of these two solutions toward alkali also appeared to be different. The addition of one drop of 0.05 *N* sodium hydroxide to 10 cc. of B produced a deep blue color which faded in a few minutes to a yellowish green. With

² Szu-chih Liu and Hsien Wu, *THIS JOURNAL*, 54, 791 (1932).

³ W. M. Clark, "The Determination of Hydrogen Ions," Williams and Wilkins Co., Baltimore, Md., 1920.

A, on the other hand, several times as much alkali was required to produce the blue color, and this turned rather quickly to yellow. On standing in Pyrex glass for a few days, B required more sodium hydroxide than A to produce the same color. The commercial indicator therefore probably is inhomogeneous, which is not surprising in view of the complicated structure of this molecule.

When a small amount of freshly prepared solution A, to which sufficient sodium hydroxide had been added to give a blue green color, was divided into two parts, one of which was kept for a control and the other subjected to radiation, the radiated sample quickly turned yellowish green and then yellow. When more sodium hydroxide was added to this sample, the blue-green color was reestablished. Further radiation again turned this yellow. This process was repeated several times but the color became less intense until finally all the dye molecules were destroyed. This completely confirmed the results reported by Schmitt, Johnson and Olson.

With a fresh solution of B, on the other hand, the radiated sample gradually faded in color without turning yellow so that after half an hour's exposure the solution was water white. The addition of alkali did not cause a return of color, which is in accord with the observations of Szu-chih and Hsien Wu.

In order to determine whether this difference in behavior was due to differences in hydrogen-ion concentration or whether it was due to difference in the characteristic end-points of the two samples of indicator, the experiments were repeated using hydrogen electrodes to determine the change in the hydrogen-ion concentration. Two hydrogen electrodes were used, one in the radiated sample and one in the control. The two samples were connected by a bridge which was fitted with a stopcock that was opened only when readings were taken.

Under these conditions it was found that when solution A was radiated until it turned yellow, the hydrogen-ion concentration was 2.5 times that of the control. On the other hand, when solution B was radiated until the color faded, its hydrogen-ion concentration was 5 times that of the control, thus showing that solution A was much more sensitive to the hydrogen-ion concentration than solution B.

In the work of Szu-chih Liu and Hsien Wu the indicator for their samples was taken from a 0.0006 *M* solution which they had made, but 20 drops were used per 100 cc. in the solution subjected to radiation so that their indicator concentration was 5 times that normally used for titration or about 1.7×10^{-5} *M*. This corresponds to one-tenth the concentration of solution C.

If the *P_H* of a solution of pure C is adjusted to slightly above the 7.6, possibly around 8, then the color fades slowly and does not give the yellow acid color. Upon radiation various dilutions of solution C were then

tried, starting in each case with the P_H color for 7.2 and it was found that the yellow color was obtained down to a composition of 4 cc. of solution C with 46 cc. of water and 2 drops of 0.05 N sodium hydroxide. With this solution and those more dilute than 0.000015 M of indicator, the indicator was apparently decomposed without change of color. With a P_H of 7.6 it required a much greater concentration of indicator to produce a yellow color. These results confirm the explanation offered above for the apparent discrepancy between the two investigations.

Tests were then made to detect whether the vibrations had a direct or an indirect effect upon the indicator by adjusting a basic solution to such a value that the 7.2 P_H color was given upon the addition of an equal volume of solution C. Samples of this were put in three test-tubes which had been carefully rinsed with the solution. To one was added the indicator solution and this colored one along with a clear one was placed in the vibrating carbon tetrachloride. After ten minutes' radiation the samples were removed and all three brought to the same temperature. The indicator solution was then added to the other two samples. That sample which was exposed with the dye present in solution showed the usual change in color to the acid side and the clear solution which was exposed likewise showed more acid but not so great as in the first case.

This demonstrates rather conclusively that the vibrations produce effects in addition to those produced on the indicator molecules, such as hydrogen peroxide formation as suggested by Schmitt, Johnson and Olson or solution of, or adsorption by the glass.

A solution of indicator which has turned yellow due to ultrasonics can be restored to the green color by boiling so that the presence of a volatile acid is indicated. Such a solution can again be made acid by further radiation and the volatile acid again removed. Each time this is done the color is less pronounced. The process can be repeated until the color is completely destroyed. This definitely removes the possibility that the carbon dioxide of the air can be entirely responsible for the color change.

Conclusions

It has definitely been shown that the observations of Szu-chih Liu and Hsien Wu and of Schmitt, Johnson and Olson are not necessarily in conflict and that the variation of indicator and hydrogen-ion concentrations presents one explanation of the differing results.

There is also the possibility that the brom thymol blue obtained for use as indicator is not a homogeneous substance and that the compounds used by the two sets of experimenters differed.

The results definitely prove that the hydrogen-ion concentration does change upon the destruction of the indicator.