

5. Mono- and dibutylamines, malonic ester, and acetoacetic ester react with ammonia solutions of iodine. No definite compounds were isolated from the reaction products.

6. Benzene, ethylene, trimethylethylene, propylene, pentane, and triphenylmethane do not react with iodine under the conditions studied.

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## EFFECT OF ULTRASONIC RADIATION ON INDICATORS

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RECEIVED SEPTEMBER 29, 1931

PUBLISHED FEBRUARY 5, 1932

In a study on oxidations promoted by ultrasonic radiation, Schmitt, Johnson and Olson<sup>1</sup> found 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 became yellow in a very short time. Since the addition of alkali caused a prompt return of the blue color they concluded that comparatively few of the dye molecules were destroyed but they were "altered by the radiation and give rise to hydrogen ions." This seems to us a very significant finding, and we have repeated and extended their experiments. Unfortunately our results do not confirm theirs.

### Experimental

The oscillating current was generated by two 75-watt tubes (UX852) connected in a modified Hartley circuit. The quartz plate (about  $47 \times 50$  mm.) lay between two brass electrodes, the distance between which could be adjusted. The vibrating part was placed in a dielectric liquid, xylene or benzene. The quartz plate vibrated at the rate of  $1.3 \times 10^6$  times per second. On the upper electrode was placed a cooling coil of glass tubing through which cold water circulated.

Indicators used in this investigation were: thymol blue, brom phenol blue, brom cresol green, chlor phenol red, brom cresol purple, brom thymol blue, phenol red, congo red, methyl red, litmus, alizarin red and methyl violet.

About 15 cc. of dilute aqueous solution of each indicator (3 drops of 0.04% indicator solution in 15 cc.) was placed in a small, thin test-tube 15 mm. in diameter. The tube was held so that its bottom was just buried in the mount of the vibrating dielectric. After exposing for ten minutes, the tube was taken out and its color compared with that of the unexposed control. The temperature of the indicator solutions never rose above 35°.

<sup>1</sup> Schmitt, Johnson and Olson, *THIS JOURNAL*, **51**, 370 (1929).

1. **Unbuffered Solutions.**—Unbuffered solution of each indicator was adjusted to show an alkaline reaction such that the addition of one drop of  $N/10$  hydrochloric acid would cause it to show an acid reaction, or a distinct change of color. After an exposure of ten minutes, the color of all indicator solutions became lighter than the unexposed control. Some of them even turned colorless but none showed acid color. The exposed solution of each indicator was, then, divided into two equal portions. To one portion were added two drops of  $N/10$  sodium hydroxide and the resulting color compared with the other portion as control. It was found that addition of sodium hydroxide did not cause a return of the original color. If the change in color were due to hydrogen ions formed by ultrasonic radiation, two drops of  $N/10$  sodium hydroxide would certainly be enough to neutralize them. The control portion of each radiated solution was left to stand overnight, and none of them showed a return of the original color. This observation shows that the indicator molecules are permanently destroyed by radiation.

2. **Buffered Solutions.**—The indicator solutions were buffered to show an alkaline reaction. They were radiated for ten minutes, and the color faded just as in the case of the unbuffered solutions. This shows that color fading is not due to the change of  $P_{\text{H}}$  of the indicator solution.

3. **Gas-free Unbuffered Solutions.**—Vigorous cavitation of the dissolved air from the radiated solution suggests that oxidation might be the cause of the destruction of indicator molecules, since Schmitt, Johnson and Olson have obtained positive tests for the presence of hydrogen peroxide in the radiated solution. To test this hypothesis the indicator solutions were made gas-free before radiation. This was done by boiling the indicator solutions for five minutes in small test-tubes and then a layer of liquid paraffin was laid on the surface. The gas-free solutions, when radiated, showed no change of color.

4. **Unbuffered Solutions Saturated with Oxygen or Hydrogen.**—Indicator solutions made gas-free by boiling were saturated with oxygen or hydrogen after cooling. With oxygen, color faded very rapidly when the solution was radiated and the addition of two drops of  $N/10$  sodium hydroxide did not cause a return of the original color, but no fading of color was observed in solutions saturated with hydrogen.

The above observations show conclusively 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 hydrogen-ion concentration. Since only solutions containing air or oxygen show color fading, the destruction of the indicator must be due to oxidation. It would seem that the traces of hydrogen peroxide which Schmitt, Johnson and Olson have detected might be

responsible for the oxidation, but we have added large amounts (1 cc. of 2% solution) of hydrogen peroxide to 15 cc. of the dilute indicator solution without observable effect. It is probable that the dissolved oxygen is directly activated by ultrasonic radiation.

### Summary

Twelve unbuffered indicator solutions, saturated with air or oxygen, showed color fading when exposed to ultrasonic radiation. Buffered solutions gave the same result. The color of gas-free solutions and solutions saturated with hydrogen did not fade when exposed. These observations show that indicator molecules are permanently destroyed by oxidation under the influence of ultrasonic radiation.

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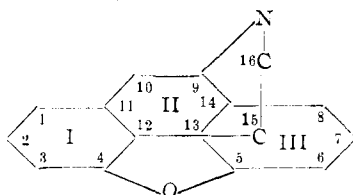
## DESOXYCODEINE STUDIES. III. THE CONSTITUTION OF THE SO-CALLED $\alpha$ -DIHYDRODESOXYCODEINE: BIS-DIHYDRODESOXYCODEINE<sup>1</sup>

BY ERICH MOSETTIG, FRANK L. COHEN AND LYNDON F. SMALL

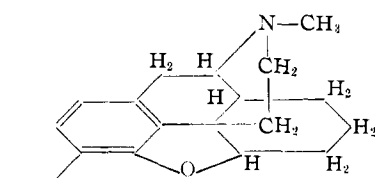
RECEIVED SEPTEMBER 29, 1931

PUBLISHED FEBRUARY 5, 1932

In the second paper of this series<sup>2</sup> five isomeric dihydrodesoxycodeines were described, of which four are phenolic in nature, and the fifth (dihydrodesoxycodeine-D) still contains the codeine cyclic ether structure intact (formula II).



I. Numbering system



II. Dihydrodesoxycodeine-D

Dihydrodesoxycodeine-D represents the only possible non-phenolic member of this class, provided no isomerism appears as a result of steric differences at the asymmetric carbon atoms 5, 9, 13 or 14. Nowhere in morphine chemistry is there any convincing evidence which warrants the expectation of such a stereoisomerism.<sup>3</sup>

<sup>1</sup> This investigation was supported by a grant from the Committee on Drug Addiction of the National Research Council from funds provided by the Bureau of Social Hygiene, Inc.

<sup>2</sup> Small and Cohen, *THIS JOURNAL*, **53**, 2227 (1931).

<sup>3</sup> Ref. 2, pp. 2231, 2232.