

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BOSTON UNIVERSITY]

**THE PHOTOCHEMICAL ACTIVITY OF THE TRIPHENYL-  
METHANE SULFONIC ACIDS**

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**Introduction**

It was accidentally discovered that Schiff's reagent contained in a clear quartz flask developed a color, apparently that of the magenta, when exposed to ultra-violet light from an iron arc. However, when the flask was removed from the light the color slowly disappeared.

At the time of its discovery, no similar reactions could be found in chemical literature but as the contents of foreign journals became available, it was seen that a reaction of the same nature had been found by Lifschitz and Joffe.<sup>1</sup> These investigators decolorized triphenylmethane dyes with potassium cyanide and brought back the color on exposure to ultra-violet light.

**Experimental**

**Reaction General to Triphenylmethane Dyes.**—Attempts to reproduce this reaction with a newly prepared portion of Schiff's reagent were unsuccessful at first. However, it was soon found that the concentration of the sulfurous acid had to be very low in order that the reaction take place.

All other triphenylmethane dyes at hand were tried, consisting of malachite green, methyl violet, and crystal violet, and in each case the colorless sulfurous acid solution developed the color of the dye on exposure to ultra-violet light in a clear quartz test-tube. From these results the writer assumed that the transformation must be general to this class of dyes as the explanation of the phenomenon will show, must be the case.

**Color Developed Same as That of the Dye in Solution.**—Although to the eye the color of the dyestuff in solution and that developed by the colorless sulfurous acid solution of the dye under the influence of ultra-violet light were apparently the same, the absorption spectra of the two were compared.

**Method.**—The absorption spectrum of the dye was obtained in the usual manner by passing the light from an incandescent gas mantle through a test-tube containing a solution of the dye; and the transmitted light analyzed in a Hilger direct-reading spectroscope. However, in the case of the sulfurous acid solution of the dye, a quartz test-tube was used, and in order that the maximum color be maintained while the measurements were being made, the light from an iron arc played on the test-tube from one side.

<sup>1</sup> Lifschitz and Joffe, *Ber.*, **52B**, 1919-26 (1919); *C. A.*, **14**, 1984 (1920).

**Results.**—By this method, the bands of the dyestuff and those developed by the sulfurous acid solutions of the dye under the influence of ultra-violet light were found to be identical. In some cases the color tone was not the same to the eye. This led to the belief that there may be side reactions to a very slight extent with the formation of some other colored substances.

**Influence of Concentration of Acid on Intensity of Color Developed.**—With solutions of dye in conc. sulfurous acid no effect could be obtained. When the solution was boiled so as to reduce the concentration of the acid, the color appeared on boiling but disappeared again on cooling. This effect has already been noticed by a number of observers. However, the cooled solution was active, giving color on exposure to ultra-violet light, and as more sulfur dioxide was boiled off, it became increasingly so. This fact led to the belief that the amount of color developed might be inversely proportional to the concentration of the sulfurous acid. With this in mind, a number of quantitative measurements were made, and the results plotted in the form of curves in Fig. 1.

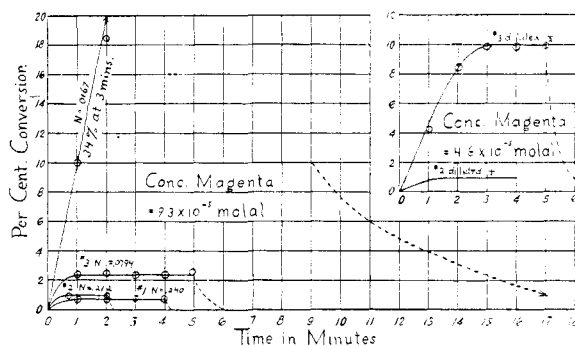


Fig. 1.—Relation of maximum color to acid concentration.

**Procedure.**—A solution of magenta of known concentration was prepared and rendered colorless by passing in sulfur dioxide. The excess of sulfur dioxide was boiled off and the strength of the residual acid determined by titration.

A portion of this solution was placed in the quartz reaction tube and exposed to the ultra-violet light from an iron arc. The amount of colored dyestuff ion formed, which is denoted in our figures by percentage conversion, was measured by comparing the color in the quartz tube with a series of standards made from the dye itself. Owing to the unevenness of the quartz tube, the color measurements could be obtained to an accuracy of only a few per cent., but this was near enough to show the shape and form of the curves. The percentage of decolorized magenta con-

verted into the colored dye was plotted along the abscissa against time along the ordinate.

Conductivity methods were not used to determine this conversion owing to the danger of photochemical effects at the electrodes of the conductivity cell. Furthermore, great inaccuracy would be introduced owing to the difficulty in measuring the very slight change in conductivity which is caused by the formation of ions from the decomposed magenta sulfonic acid (of small concentration), in the presence of such a relatively large amount of sulfurous acid.

Fig. 1 shows the curves obtained, the solid line representing the conversion into the colored form when the arc was running, and the dotted line that after the arc had been turned off.

One will notice that the smaller the concentration of the sulfurous acid, the steeper the curve and the larger the conversion. Moreover, with high concentrations of acid the color faded almost immediately, but with low concentrations it faded very slowly, sometimes taking a number of hours (not shown in the curves). Curves 2 and 3 (in insert) illustrate the results obtained when the solutions were diluted with equal amounts of water.

All the curves indicate that there is some sort of an inverse relation between the maximum color obtained and the concentration of the sulfurous acid. As the experimental error was necessarily large, the results are not good enough to determine accurately the nature of this relation.

The results up to date indicate that there are two reactions taking place: (1) a decolorizing reaction whose velocity is proportional to the concentration of the sulfurous acid or at least closely related to it; and (2) a colorizing reaction in the opposite direction whose velocity is in all probability proportional to the intensity of the ultra-violet light.

### Effect of Intensity of the Light

If the above interpretation be correct then the maximum color developed

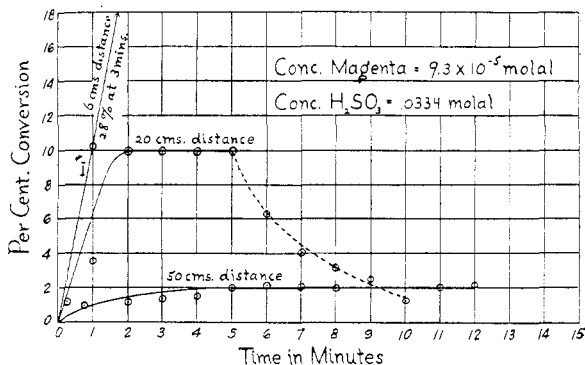


Fig. 2.—Maximum color vs. intensity of light.

should be proportional to the intensity of the light. To test this point a solution of decolorized magenta of known concentration was exposed to the rays of an iron arc at 6 cm. distance and the rate of formation of color plotted as shown in Fig. 2, Curve 1. The maximum color obtained was so intense that it was impossible by the method used in comparing colors to obtain a reading.

The solution was allowed to decolorize and then was exposed again at 20 cm. distance. The velocity was much less than in the former case and the maximum color was obtained in about 2 minutes. Again the tube was removed from the light and the color allowed to fade. It was then exposed at 50 cm. distance. The maximum color in this case was of a very low order, as can be seen from the curve.

Taking the maximum amount of color at 50 cm. distance and calculating the maximum color at 20 cm. distance, assuming that the maximum color developed is proportional to the intensity of light, we find it should be 12.5% conversion. From the curve we see that the amount actually measured is 10% which is in agreement within our experimental error. Hence the coloring reaction must be photochemical, as its rate and the maximum color developed are proportional to the amount of light absorbed.

### Relation Between the Maximum Color and the Concentration of the Magenta

Two solutions were made up having different concentrations of magenta but the same of sulfurous acid. They were then exposed to the light until a maximum color was developed.

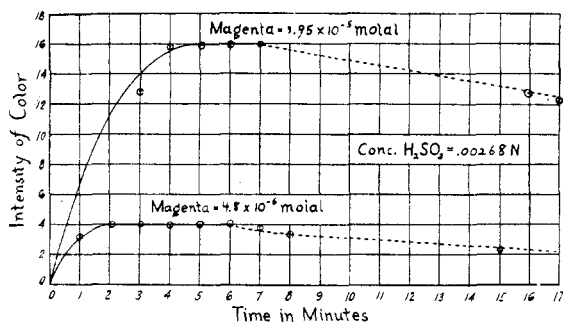


Fig. 3.--Maximum color vs. concentration of magenta at some acid concentration.

Fig. 3 shows the results in the form of two curves. The concentration of the magenta in one case was four times that in the other, and the color developed in the stronger solution was four times that in the weaker, showing a direct proportion between color and concentration of magenta.

### Maximum Color and Free Sulfurous Acid

Very remarkable results were obtained when a solution of decolorized magenta was exposed to the ultra-violet light and neutralized in steps by the addition of alkali from a buret above the reaction tube, the color being compared with a series of standards after each addition of alkali.

At certain small concentrations of sulfurous acid a maximum color was obtained instead of at the neutral point, as would be expected. After passing the maximum point, the color faded rapidly, and when the solution was neutral the color had entirely disappeared. By adding acid in the same fashion the curve could be retraced, and could be reproduced at will from either the acid or the alkaline side. Fig. 4 shows the curves ob-

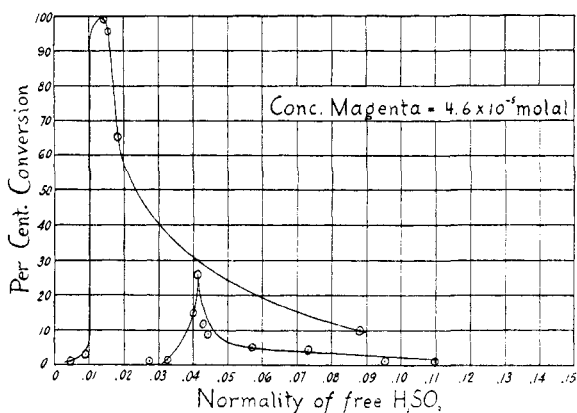


Fig. 4.—Maximum color vs. free sulfurous acid.

tained, each curve representing the same solution of magenta but having different concentrations of sulfurous acid originally present. These results can be satisfactorily explained only after further investigation.

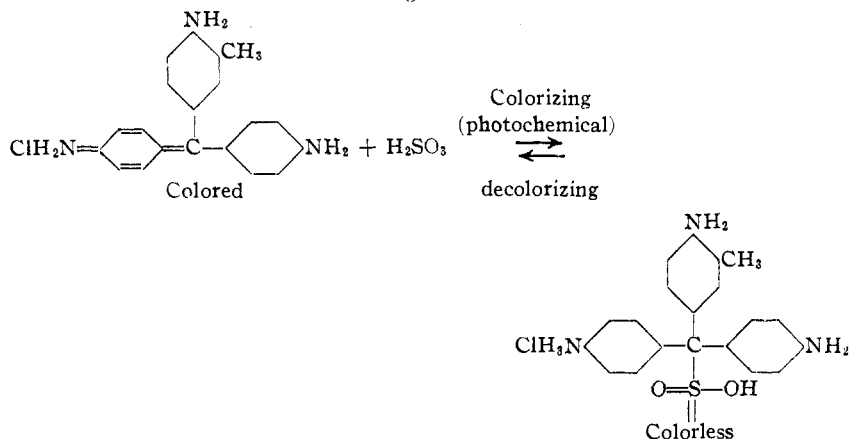
### Mechanism of the Reaction

Although the measurements were necessarily only good approximations, they leave no doubt that there are two reactions concerned in the phenomenon: (1) the decolorizing reaction taking place between the magenta and the sulfurous acid; and (2) a colorizing reaction decomposing the product formed by the first reaction which must be of a photochemical nature.

According to Hantzsch<sup>2</sup> the reaction between magenta and sulfurous acid is not a case of reduction but the formation of an addition product causing a breaking of the quinoid structure and hence the disappearance of color. A sulfonic acid is formed which is quite stable at ordinary

<sup>2</sup> Hantzsch, *Ber.*, 33, 289 (1900).

temperatures and has been isolated and analyzed. A structural representation of the two reactions is given below.



At ordinary temperatures and in daylight the point of equilibrium is far to the right as the solution is colorless. Hence the velocity of decomposition of the sulfonic acid under these conditions must be very small. However, under the influence of ultra-violet light this velocity is greatly increased, and the equilibrium is shifted towards the left, the solution becoming highly colored. The extent to which the equilibrium is shifted depends on the already mentioned factors.

This same equilibrium can also be shifted by other means. If a solution of the colorless sulfonic acid is heated, the color of the dye appears but subsequently disappears again on cooling, the reason for this being the difference in temperature coefficients of the two reactions. Moreover, by the addition of alkali the color can be made to appear as the sulfurous acid is used in neutralization and the equilibrium caused to shift to the left.

An expression for the equilibrium constant might be derived by the aid of either the Byk or the Weigert theory of photo-stationary states but as these theories are at variance in certain particulars, such an expression was not attempted. However, by making certain assumptions a simple expression can be derived the value of which remains to be determined by experiment.

**Ultra-violet Light and Heat.**—The shifting of the equilibrium which takes place at high temperatures has been caused to occur at room temperature under the influence of ultra-violet light. In terms of the quantum theory, the large quanta causing the reaction to take place are supplied by the high frequency of the ultra-violet light and added to those already present in the system, thereby increasing the radiation density and causing an increase in reaction velocity, dependent thereon. The ultra-violet light acts as "cold heat," so to speak.

**Wave Length of Light Causing the Reaction.**—There was no appa-

ratus available for the measurement of the active wave lengths causing the reaction, but inasmuch as the reaction does not take place in glass which is opaque below 3300 Å. U. and does take place in the light of an iron arc which emits nothing below 2200 Å. U., the active rays lie between these limits.

### Summary

1. Schiff's reagent was found to give a red color under the influence of ultra-violet light upon exposure in a clear quartz tube.
2. Other triphenylmethane dyes that had been decolorized by sulfur dioxide, forming sulfonic acids, gave their characteristic colors under similar circumstances.
3. The color developed in each case was proved to be that of the dye itself.
4. It was shown that there were two reactions taking place: (1) a decolorizing reaction; and (2) a colorizing reaction which is photochemical.
5. The large quanta supplied by the ultra-violet light cause the velocity of the photochemical reaction to increase; hence a shifting of the equilibrium takes place.
6. The equilibrium in this system can be shifted by chemical and thermal as well as photochemical means.

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## A REVISION OF THE ENTROPIES OF THE ELEMENTS

BY GILBERT N. LEWIS, G. E. GIBSON AND W. M. LATIMER

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In the future development of thermodynamic chemistry it is probable that some of the greatest advances will be made through two new thermodynamic principles.

The first of these is known as the Third Law of Thermodynamics, which, when stated with proper caution,<sup>1</sup> may now be regarded as one of the exact laws of nature. Such doubt as may have existed regarding the adequacy of its experimental verification we believe will be resolved by the further and more precise evidence which is to be adduced in the present article.

<sup>1</sup> See Lewis and Gibson, "The Third Law of Thermodynamics and the Entropy of of Solutions and of Liquids," [THIS JOURNAL, **42**, 1529 (1920)]. A more complete statement of the third law is given by Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill, New York (in press).