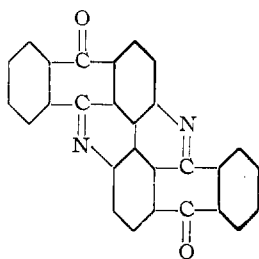


THE REDUCTION OF AN INDANTHRENE DYE BY MEANS OF SODIUM HYDROSULFITE

BY JOHN H. YOE AND GRAHAM EDGAR¹

I. Introduction

Dyes of the indanthrene series are usually applied to the fabric in the reduced condition, reduction being effected by an alkaline solution of sodium hydrosulfite. Although the most favorable conditions for practical use of these dyes are very well known, relatively little seems to have been established as to the mechanism by which the reduction occurs, and the influence of different factors upon the rate of the reaction. The experiments discussed below were carried out with the object of throwing some light upon this problem. The dyestuff chosen for the investigation was an oxyindanthrene of the formula



furnished by the Du Pont Company, and known by them as Ponsol Yellow G. The sample was of high purity.

II. Experimental

Some preliminary experiments were carried out under the microscope by mixing a little of the dye with a drop of NaOH solution, and then allowing a solution of NaHSO₂ to diffuse into the mixture. When the NaHSO₂ reached the dye crystals a growth of small dark blue needles began to cover them

¹ Contribution from the Cobb Chemical Laboratory of the University of Virginia.

and these began slowly to go into solution giving to the mixture the characteristic dark blue color of the reduced dye. These experiments indicated that the actual reduction of the dye is a rapid reaction, but the rate of solution of the reduced dye is much less rapid.

More exact experiments were then designed to measure the rate of reduction and solution of the dye. Since the rate of a heterogeneous reaction is in general largely dependent upon the surface, it was decided to compress the dye into disks having an approximately constant surface. The apparatus finally developed for the work is illustrated in Figure I. The disk of compressed dye was formed by forcing a steel plunger into a steel cylinder of 9.5 mm diameter, containing a sufficient quantity of the dye crystals. The disk was then fitted into a flat container, so adjusted that 0.5 mm of dye projected above the edge of the container. The container was placed in the bottom of a liter beaker, being adjusted so as to take up a position half way between the center and wall of the beaker.

The beaker was fitted with a wooden cover provided with holes through which the stirrer and thermometer passed, and others through which hydrogen gas could be introduced and samples for analysis withdrawn. The stirrer was adjusted so that the arms were exactly 1 cm above the disk, and its speed was kept constant at 500 r.p.m. The beaker was immersed in a thermostat at 25°C (± 0.02).

The procedure observed in carrying out a determination was as follows: the disk of dye was placed in the beaker and the complete apparatus set up. The air in the beaker was then replaced by hydrogen, the stirrer was set in motion, and 500 cc of alkaline NaHSO_2 solution, previously warmed to 25°C was then added. At frequent intervals the amount of reduced dye in solution was determined by withdrawing a 10 cc sample of the solution, diluting it with a solution containing NaOH and NaHSO_2 and comparing its color with that produced by reducing completely a known weight of the dye. A Sargent colorimeter was used. Experiment showed that

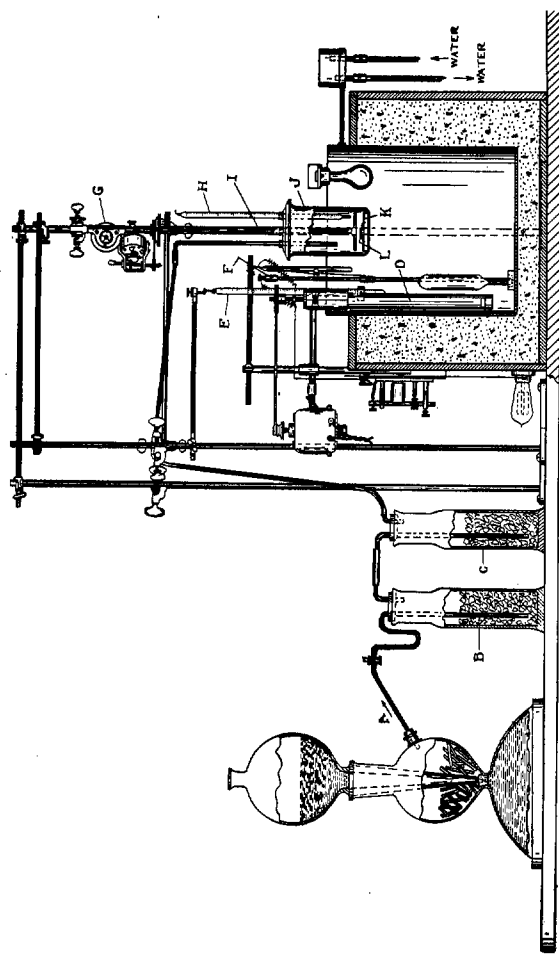


Fig. 1

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|----------------------------------|----------------------|-----------------------|
| A = Hydrogen | E = Bath Thermometer | I = Vat Stirrer |
| B = Sodium Hydroxide Solution | F = Thermo-regulator | J = Reduction-Vat |
| C = Alkaline Pyrogallol Solution | G = Speed Indicator | K = Dye Tablet Holder |
| D = Bath Stirrer | H = Vat Thermometer | L = Dye Tablet |

the color of the solution was exactly matched to the eye by cobalt glass, and in many cases plates of this glass, calibrated against weighed amounts of the dye, were used as standards. The dye solutions were covered, while in the colorimeter, with a thin layer of oil, to prevent atmospheric oxidation.

The experiments were usually continued until the rate of reaction became very slow. In some cases irregularities were caused by partial disintegration of the dyestuff disk, but these experiments were discarded from consideration. Examination of the disk at the end of an experiment always showed it to be covered by a layer of blue solid, confirming the preliminary indications that the rate of *solution* is the slow factor in the reaction.

The concentrations of NaOH and NaHSO₂ were varied separately, and in one experiment NaCl was added.

Characteristic experimental data are given in Table I, and are expressed graphically in Figures 2 and 3.

TABLE I
Reduced Dye in Solution, mg per litre
(Temp. = 25° C; Stirrer = 500 r.p.m.; 5 gm NaHSO₂)

Conc. NaOH	0.18 N	0.36 N	0.72 N	1.08 N	1.44 N	2.88 N
Time (min.)	Concentration of Reduced Dye (mg per liter)					
10	—	70	48	—	18	—
20	—	91	82	36	25	—
30	28	108	99	54	31	11
40	30	121	109	67	36	—
50	31	130	122	77	42	—
60	32	135	126	85	48	20
70	33	136	127	91	53	22
80	34	137	128	96	59	23
90	35	137	129	99	63	24
100	36	137	129	103	68	25
110	37	137	—	106	71	26
120	38	137	—	109	74	26
130	39	—	—	110	75	27
140	40	—	—	111	76	28
150	40	—	—	111	76	29
160	41	—	—	112	76	29

On attempting to duplicate the experiments under any given conditions it was found that whereas results of the same general character were invariably obtained, the rate of solution and the final maximum amount of dye going into solution varied considerably in individual experiments. In the light of final conclusions discussed below, it seems probable that these variations are largely determined by unavoidable differences in the degree of compression of the dye disk. It is felt that these variations are not sufficient to affect the general conclusions drawn. The data given have been selected as typical.

III. Discussion of Experimental Data

(a) General Nature of the Reaction Velocity Curves.

Examination of the curves of Figure 2 shows that they all consist of the same general type,—a fairly rapid initial rate of solution, followed by a gradual slowing up of the rate, until finally the reaction practically ceases. In fact, it would at first appear that the process represented the simple solution of a solid, the rate of which is in general determined by the rate of diffusion of the dissolved solid,^{1,2} and follows the expression³

$$K = \frac{V}{t_2 - t_1} \ln \frac{S - c_1}{S - c_2}$$

where V represents the total volume; t_2 and t_1 , time intervals; c_2 and c_1 corresponding concentrations, and S the concentration of the saturated solution.

Further consideration, however, makes it apparent that we are not dealing with a simple solution phenomenon, determined by the rate of diffusion. In the first place the great effect of the concentration of sodium hydroxide on the rate (see further below) cannot be accounted for on the diffusion hypothesis, as a relatively small increase in the concentration

¹ Noyes and Whitney: *Zeit. phys. Chem.*, **23**, 689 (1897).

² Nernst and Brunner: *ibid.*, **47**, 52 and 56 (1904).

³ Van Name and Edgar: *Am. Jour. Sci.*, **29**, 237 (1910).

of NaOH can hardly be expected to double the rate of diffusion of the dissolved dye. In the second place experiments showed that the apparent limit reached by the reaction does not represent a true solubility of the reduced dye, for after the *disk* had practically stopped dissolving, the apparently saturated solution would dissolve considerable quantities of *finely divided dye*. We can therefore dismiss the idea that the reaction

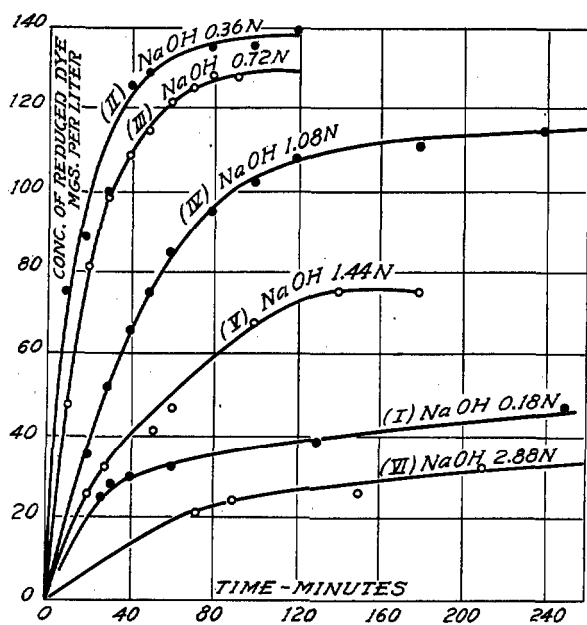


Fig. 2
Effect of Alkali Ion

consists merely of a rapid reduction of the dye, followed by simple solution of the reduced dye.

(b) The Effect of Sodium Hydroxide.

The effect of sodium hydroxide on the rate of reaction is most marked. In the curves of Fig. 3 the concentrations of reduced dye have been plotted as ordinates, and concentrations of alkali as abscissas, separate curves being drawn for

the different time intervals. It will be noted that a pronounced maximum occurs between normalities of 0.24 and 0.72, apparently in the neighborhood of 0.5N. In an experiment with 5 normal NaOH the rate was so slow as to preclude measurement. The character of the curves of Fig. 3 suggests that

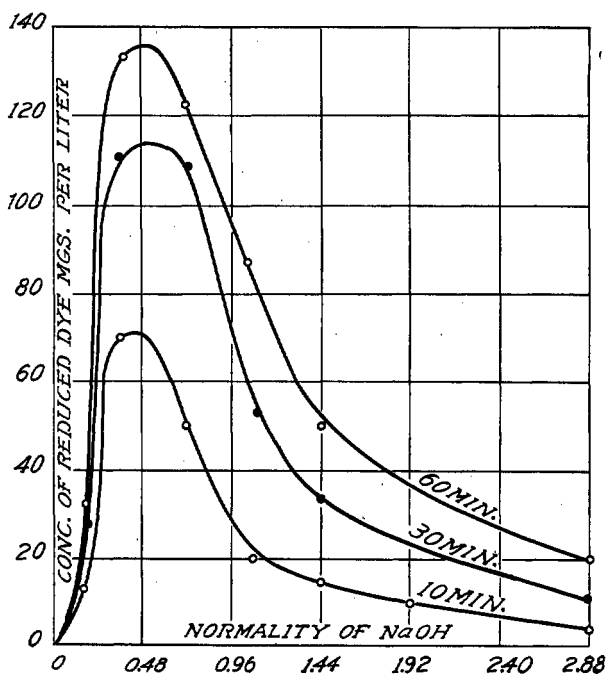


Fig. 3

Effect of Alkali Ion
Conc. Dye vs. Normality of NaOH at Constant Time

hydroxyl ion may favor the rate of solution while sodium ion retards it. Additional data on this point were secured by carrying out an experiment similar to those of Table I, except that the solution was 0.36N in NaOH and 2.52 in NaCl. The rate of reaction was even lower than that in which 2.88N NaOH was employed, although the normality of the NaOH was approximately that giving the maximum rate when pres-

ent alone. The bearing of these facts on the probable mechanism of the reaction is discussed below.

(c) The Influence of NaHSO_2 .

A series of experiments was carried out in which the concentration of NaOH was kept constant at 0.72N, and the amount of NaHSO_2 varied between 1 and 30 grams per 500 cc of solution. The results show a very slow rate of reaction when only 1 gm was present but relatively little difference between the rates in solutions containing 5, 20 and 30 grams. Provided a considerable excess is present, therefore, it does not seem that the NaHSO_2 materially affects the rate of reaction.

(d) Effect of Rate of Stirring.

Two parallel experiments were carried out in which the rate of stirring was 400 and 500 r.p.m., respectively. The result indicated an increase in the rate of solution of about 10% when the rate of stirring was increased from 400 to 500 r.p.m.

(e) Indications of the Colloidal Nature of the Reduced Dye.

The experiments outlined above suggested the probability that the reduced dye is really in colloidal suspension rather than in true solution, and that we are dealing with a peptization phenomenon. A few additional facts tend to support this theory. Filtration of the alkaline reduced solution through several layers of hardened filter paper gave a filtrate at first water-clear and colorless, while a layer of the blue reduced dye was found adhering to the filter paper.

The reduced dye solution is readily precipitated (coagulated) by various inorganic salts.

In the field of an improvised ultramicroscope large numbers of ultramicros were observed. It was, however, found impossible to prepare an optically void solution of the alkaline hydrosulfite, so that this result cannot be taken as conclusive.

IV. Conclusions

Considering all of the data discussed above we are led to the conclusion that the reduction and solution of the dye-stuff in question (and probably others of the same type) in-

volve (a) the rather rapid reaction of the dye with the alkaline hydrosulfite to form an insoluble crystalline reduced dye; and (b) peptization of the reduced dye through the agency of the hydroxyl ions, the resulting solution being colloidal in nature. The rate of solution and the *amount* of *dyestuff* which will be peptized by a given solution, depends upon the state of subdivision of the dye. Positive ions tend to coagulate the solution, and to retard the peptization of the reduced dye.

It is realized that these conclusions are based on data perhaps in themselves not entirely conclusive, but it has not been possible to make any other explanation account for the observed facts.

V. Summary

- (1) Measurements have been made of the rate of reduction of an indanthrene dye by alkaline hydrosulfite solutions.
- (2) The influence of various factors has been determined.
- (3) The results indicate that the rate of reduction of the dye is rapid, but the "solution" of the reduced dye is in reality a peptization by alkali.

University, Virginia