

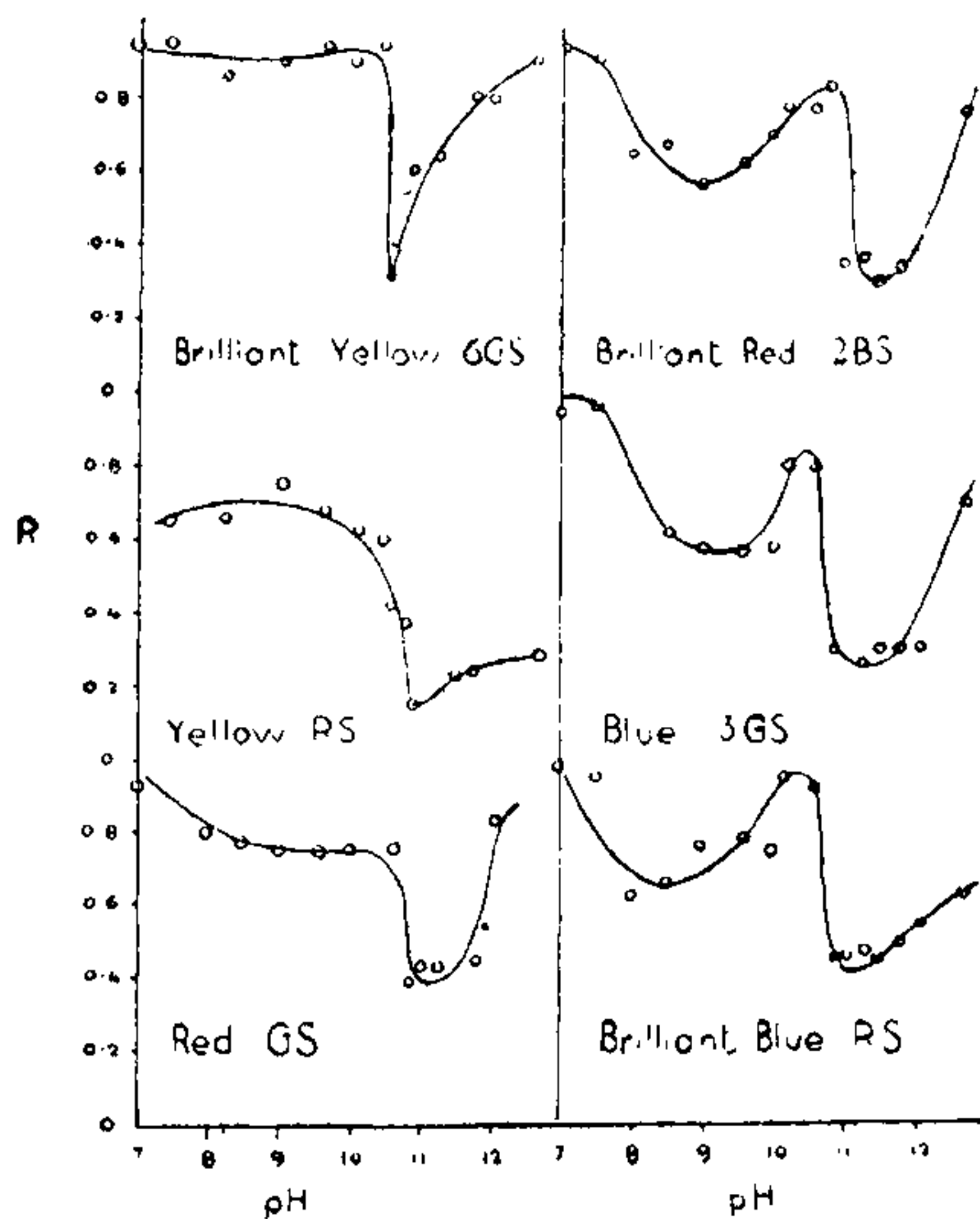
A CHROMATOGRAPHIC STUDY OF SOME REACTIVE DYESTUFFS

RECENTLY chemically reactive dyestuffs have been put on the market by I.C.I., Ciba and Farbwerke Hoechst under the trade names Procion, Cibacron and Remazol respectively. These dyes¹⁻³ all have the common characteristic of forming a chemical linkage with cellulose but only in alkaline media, the rate and extent of reaction being dependent on pH and temperature. In alkaline solutions the dyes also undergo hydrolysis forming what are called inactive dyes and which have practically no substantivity for cellulose, a property which is also shared by the active dyes when in neutral solutions.

In view of these unique properties of reactive dyes it was thought that a circular paper chromatographic study of these dyes as a function of pH using cellulose filter-paper would lead to some interesting results. Chromatograms under identical conditions were therefore taken on 12.5 cm. diameter Whatman No. 1 filter-paper discs using Rutter's method.⁴ The developing solutions were buffer mixtures covering the pH range 6.9-12.7. Cold brand Procion dyestuffs were used in these experiments. These highly reactive dyestuffs contain two labile chlorine atoms of relatively high reactivity and are formed by linking cyanuric chloride with water soluble azo or anthraquinone dyes that contain an amino group. These two labile chlorine atoms are available for combination with cellulose.^{1c} 0.2% aqueous solutions of the commercial dyes were used in all the experiments. After marking the positions of the different zones the chromatograms were soaped and boiled in order to remove inactive hydrolysed dye. R values for chemically combined dye were measured in all cases, R being defined as the ratio of distance travelled by dye to that travelled by the solvent front in the same time. The variation of R with pH is presented graphically in Fig. 1.

During the development of the chromatogram the adsorbed dye can react partly with the cellulose of the filter-paper forming a chemically fixed coloured zone, get hydrolysed partly to the inactive form and while the developing solvent advances, unreacted active dye and the hydrolysed inactive dye will diffuse out forming outer coloured zones of further chemically combined dye and loosely bound physically adsorbed inactive dye respectively. The Procion dyes studied show this expected behaviour when chromatographed. The extent of spread of the zones and the formation of

more than one chemically combined zone is dependent on the relative reactivities and affinities of the dye for cellulose as well as the pH of the eluting solvent.



VARIATION OF R VALUES WITH pH FOR PROCION DYES. TEMPERATURE: 23 ± 1°

FIG. 1

From Fig. 1 it is clear that R has minimum values depending on pH. For Procion Yellow RS, Brilliant Yellow 6GS and Red GS there is a single sharp minimum value for R and it is interesting to note that the pH corresponding to this minimum R value is almost identical with the optimum pH value for percentage maximum fixation of the dye on cotton in the same temperature range.⁵ In the case of Procion Brilliant Red 2BS, Brilliant Blue 3GS and Blue RS, R is a minimum at two or more pH values. These minima are not sharp and also there is no specific correlation between the value of optimum pH for maximum percentage fixation and the pH corresponding to a minimum R value, but it is noteworthy that Procion Brilliant Red 2BS has peak fixation values at more than one pH value.⁵ At high alkali concentration it is clear that the reaction between these dyes and cellulose is quite complex. A general conclusion which can be drawn from the data obtained is that the rate of reaction with cellulose is governed by several factors and is not always instantaneous,^{1a} since zones of chemically combined dye

having high R values are obtained both at low and high pH values. A detailed study of these and other aspects of this investigation will be published elsewhere.

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TETRAHYDROXYQUINONE AS AN ANALYTICAL REAGENT AND ITS RELATIONSHIP WITH SODIUM RHODIZONATE

SODIUM rhodizionate is an important reagent; it gives colour reactions with a large number of cations¹ and has been largely used in chromatographic spotting. Tetrahydroxyquinone is also known to give coloured products with Ba⁺⁺, Pb⁺⁺ and Sr⁺⁺.^{2,3}

Previous workers have described potassium and sodium rhodizionate as a violet crystalline compound and sodium tetrahydroxyquinone as a dark green crystalline compound.^{4,5} Hoglan and Bartow⁶ prepared both sodium tetrahydroxyquinone and sodium rhodizionate by the oxidation of inositol. These salts on acidification gave bluish black crystals, which gave the same benzoyl derivative, m.p. 266-70°. The above workers therefore doubted whether they are two different compounds.

We found that tetrahydroxyquinone reacts with a large number of cations, viz., Pb⁺⁺, Tl⁺, Ag⁺⁺, Hg⁺⁺, Ba⁺⁺, Sr⁺⁺, Ca⁺⁺, Mg⁺⁺, Bi⁺⁺⁺, Cd⁺⁺, Cu⁺⁺, Zn⁺⁺, Sn⁺⁺, and UO₂⁺⁺ and the colour reactions are the same as described for sodium rhodizionate.¹ It is very unlikely that two different compounds should give the same colour reactions with a large number of cations. We, therefore, concluded that tetrahydroxyquinone and rhodizonic acid are not two different compounds. Further we analysed a dried pro-analytical sample of sodium rhodizionate (E. Merck) and the results indicated 1% hydrogen corresponding to sodium tetrahydroxyquinone.

The following colour reactions have also been noted in neutral solutions. ZrO₂⁺⁺ red; Th⁺⁺⁺⁺ blue; Ce⁺⁺⁺ blue (Ce⁺⁺⁺⁺ oxidises the reagent).

Further, a solution of the so-called sodium rhodizionate is readily decomposed¹ being alkaline. A solution of tetrahydroxyquinone is more stable and we have observed that in the presence of a little acetic acid and formaldehyde it remains unchanged for about a week.

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BEHAVIOUR OF A MIXTURE OF NITROUS OXIDE AND HYDROGEN UNDER SPARK DISCHARGE

THE thermal reaction between nitrous oxide and hydrogen has been extensively studied.¹⁻⁴ Studies in the production of a periodicity effect under silent discharge,^{5,6} suggested the desirability of the present extension of work, viz., to investigate the reaction under spark discharge. The following experiments were conducted to find out whether a periodicity effect in the pressure vs. duration of exposure curve, similar to that observed under the silent discharge, was produced under the spark discharge.

The experimental procedure was essentially similar to that adopted earlier.⁵ The ozonizer was replaced by a glass bulb of about 50 c.c. capacity attached to the capillary manometer by a stop-cock and to the mixture reservoir (N₂O + H₂) by another stop-cock. The bulb was evacuated by the Töpler.

The results are given in Table I. The reaction under spark discharge shows an overall diminution of pressure to a constant minimum. There is a marked limitation in respect of the initial pressure of the reaction mixture (72 mm. Hg) beyond which the reaction tends to become explosive; this limiting pressure would depend upon the sparking distance, as it determines the relevant field. At higher pressure, the detonation is attended by a sudden