

## Metachromasy of Pyronine G Produced by Polyvinyl Sulfate

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In the course of the study of metachromasy,<sup>1-3</sup> we have found that Pyronine G-K polyvinyl sulfate (PVSK) system is another interesting example which can be explained almost quantitatively as due to the change of aggregation of dye ions.

Absorption spectra of Pyronine G in aqueous solutions are shown in Fig. 1. There are two maxima, which are attributed to monomer ( $\lambda$  545  $m\mu$ ,  $\alpha$ -band) and dimer ( $\lambda$  512.5  $m\mu$ ,  $\beta$ -band). From the rise and fall of these maxima accompanied with the change of dye concentration, equilibrium const. of dimerization was calculated to be  $6.38 \times 10^{-4}$  at 27°.

When PVSK is added, the change of spectra observed are as follows. (1) When the dye concentration is below  $2 \times 10^{-4}$  mole/l., the spectra do not change at all, even if large excess of PVSK is added. (2) If the dye concentration is a little above  $4 \times 10^{-4}$  mole/l., the addition of PVSK produces a new metachromatic band and at the same

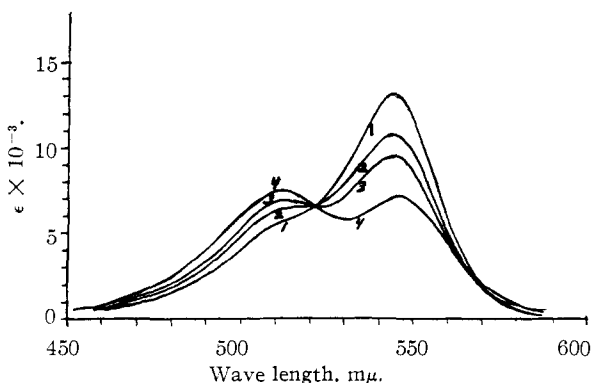


Fig. 1.—The absorption spectra of the pure aqueous Pyronine G solution, dye concentration in mole/liter, temperature, 27°: 1.  $1.5 \times 10^{-3}$ ; 2.  $2.2 \times 10^{-3}$ ; 3.  $3.6 \times 10^{-3}$ ; 4.  $4.2 \times 10^{-3}$ .

time  $\alpha$ - and  $\beta$ -bands decline apparently in a parallel way. The excess of PVSK causes the phenomenon of recovery as was observed in the case of Rhodamine 6G,<sup>1,2</sup> until the spectrum becomes quite similar to that of pure aqueous solution (Fig. 2). (3) As the dye concentration is increased, the phenomenon of recovery begins at a higher concentration of PVSK

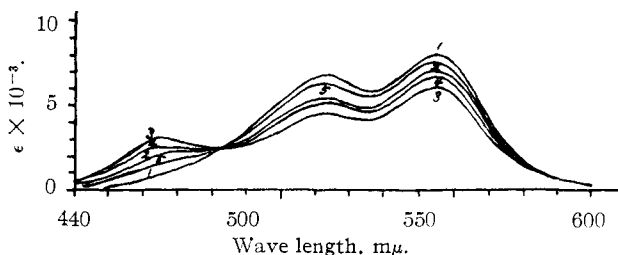


Fig. 2.—Examples of spectral change produced by the addition of PVSK dye concentration  $8 \times 10^{-4}$  mole/l. at 27°: 1. without PVSK; 2.  $5 \times 7.56 \times 10^{-6}$  g./cc.; 3.  $10 \times 7.56 \times 10^{-6}$  g./cc.; 4.  $50 \times 7.56 \times 10^{-6}$  g./cc.; 5.  $500 \times 7.56 \times 10^{-6}$  g./cc.).

and at the same time its degree is much reduced. (4) The position of the three maxima remain almost constant during the whole change.

Now the above results are explained almost quantitatively by the following simple adsorption-model. "Dye ions are adsorbed on PVSK, but neither monomer-dimer equilibrium nor their optical properties are affected by adsorption. But as the concentration of dye ions adsorbed on PVSK increases, a new molecular species, which most probably is a multiple associate of dye ions, come to existence, and it does not participate in monomer-dimer equilibrium."

It goes without saying that this model qualitatively explains the above facts. Quantitative test of the model was done as follows.

If a new molecular species is formed, the concentration of dye ions which participate in monomer-dimer equilibrium will be reduced to  $C_0 - \Delta C_0$ ,  $C_0$  being the analytical concentration. On the ground of the above model, the experimentally obtained extinction coefficient  $\lambda_m = C_0 \epsilon_m$  (at the wave length

TABLE I  
Comparison between  $\epsilon_m$  and  $\frac{(C_0 - \Delta C_0)}{C_0} \epsilon'_m$

$C_0 = 8 \times 10^{-4}$ mole/l.	$P^a$ ( $7.56 \times 10^{-6}$ g./cc.)	0	1	5	10	50	100	500	1000
	$\Delta C_0$ ( $\times 10^4$ )	0	0.1	1.6	2.0	1.4	1.4	0.1	0
	$\epsilon_m$	8.0	8.0	7.0	6.1	6.7	7.1	7.6	7.8
	$\epsilon'_m$	8.0	8.2	8.8	9.0	8.7	8.7	8.2	8.0
	$\frac{(C_0 - \Delta C_0)}{C_0} \frac{\epsilon'_m}{\epsilon_m}$	1.0	1.0	1.0	1.1	1.0	1.0	1.0	1.0
$C_0 = 10^{-3}$ mole/l.	$\Delta C_0$ ( $\times 10^4$ )	0	1.4	2.4	3.4	3.8	3.9		1.8
	$\epsilon_m$	7.7	8.2	6.75	5.7	4.5	4.9		6.3
	$\epsilon'_m$	7.7	8.0	8.7	8.8	8.9	8.94		8.0
	$\frac{(C_0 - \Delta C_0)}{C} \frac{\epsilon'_m}{\epsilon_m}$	1.0	0.8	1.0	1.0	1.2	1.1		1.0

<sup>a</sup>  $P$ ; quantity of PVSK.

(1) M. Koizumi and N. Mataga, *THIS JOURNAL*, **75**, 483 (1953).

(2) N. Mataga and M. Koizumi, *J. Inst. Polytech. Osaka City University*, **3**, 21 (1952).

(3) M. Koizumi and N. Mataga, *Bull. Chem. Soc. Japan*, **26**, 115 (1953).

of  $\alpha$ -maximum) and  $\lambda_d = C_0 \epsilon_d$  (at the position of  $\beta$ -band) must coincide with the extinction coefficients corresponding to the pure aqueous solution of which the concentration is  $(C_0 - \Delta C_0)$ .

Thus

$$\lambda_m = C_0 \epsilon_m = \epsilon'_m (C_0 - \Delta C_0)$$

$$\lambda_d = C_0 \epsilon_d = \epsilon'_d (C_0 - \Delta C_0)$$

Therefore

$$\epsilon_m / \epsilon_d = \epsilon'_m / \epsilon'_d \quad (1)$$

where  $\epsilon'_m$  and  $\epsilon'_d$  are the molecular extinction coefficients in the simple aqueous solutions.

By virtue of the relation (1), one can determine  $(C_0 - \Delta C_0)$ , and the value of  $\epsilon'_m((C_0 - \Delta C_0)/C_0)$  calculated therefrom must coincide with the experimental value of  $\epsilon_m$ , if our model is correct.

The result of the comparison is very much satisfactory as seen in Table I.

Thus the above model may be said to be quantitatively confirmed.

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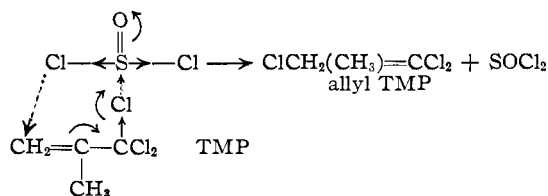
### Catalyzed Allylic Rearrangement of a 1,1,1-Trichloro-2-alkene to a 1,1,3-Trichloro-1-alkene

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1,1,1-Trichloro-2-methyl-2-propene (TMP) is rearranged to 1,1,3-trichloro-2-methyl-1-propene (allyl TMP) by the catalytic action of thionyl chloride. When a mixture of thionyl chloride and chloretonone in 5 to 1 mole ratio was heated under reflux for 30 hours,<sup>1</sup> a ratio of 88% TMP to 12% allyl TMP was obtained; but when the thionyl chloride-chloretonone mixture was heated for 48 hours, a ratio of approximately 50% TMP to 50% allyl TMP was found. By comparison, when pure TMP is heated at 100° for 48 hours, practically no rearrangement to allyl TMP occurs.<sup>2</sup>

The catalyzed allylic rearrangement of TMP is rationally explained by the following reaction path



We have also found that TMP was rearranged to allyl TMP by powdered soft glass. The TMP (90%) underwent rearrangement in 12 hours at reflux. The electron donor character of the roughened and exposed inner surfaces of the alkaline glass powder may have been responsible for catalyzing this allylic rearrangement. The electron-donor character of the present catalyst is analogous in principle to that reported for ketene acetal where this acetal also catalyzed the present type of rearrangement.<sup>2</sup>

(1) We found it necessary to employ about 30 hours reaction of chloretonone with purified thionyl chloride in order to obtain complete conversion of chloretonone to TMP. Small amounts of allyl TMP are formed. Our experience thus differs from the work of S. M. McElvain and C. L. Stevens (*THIS JOURNAL*, **69**, 2669 (1947)) in which eight hours was mentioned as sufficient for 93% yield of TMP from chloretonone.

(2) D. G. Kundiger and E. H. Freman, *ibid.*, **75**, 1744 (1953).

TMP was best separated from allyl TMP by flash distillation. In this manner an over-all accounting of 92% of the products of chloretonone was obtained (81% TMP and 11% allyl TMP) with a reaction period of 30 hours.

#### Experimental Part

**I. Reaction of Chloretonone with Thionyl Chloride.**—Purified chloretonone (1.25 moles, 222 g.) and purified thionyl chloride (5.5 moles, 654.5 g.) were heated under anhydrous conditions and under reflux (about 79°) for 48 hours, while dry nitrogen gas was passed through to remove evolved hydrogen chloride and sulfur dioxide. *Anhydrous chloretonone must be handled with special care and as rapidly as possible because of its extreme hygroscopicity.* The unreacted thionyl chloride was distilled off through a packed column under 140 mm. pressure. The residual liquid was transferred to a Claisen flask and distilled to give 150.9 g. (75.7%) of a 50-50 mixture of TMP and allyl TMP, b.p. 130-158° (the b.p. of TMP is 130-137°; the b.p. of allyl TMP is 152-158°). This mixture was preceded by a forerun of 7.5 g. which boiled largely at 125-130°. Note: Porcelain boiling chips prevented quite well the troublesome bumping and frothing always experienced with the distillation of the TMP-allyl TMP mixture. Use of a fairly large capillary ebulliator tube through which a slight stream of dry air is drawn with slight suction on the system is preferred. This product ratio was not changed by refluxing the 50-50 mixture for 3 hours or by refluxing in the presence of hydrogen chloride for 30 minutes.

**Conversion of Chloretonone to TMP.**—The following experiment was designed to yield the maximum TMP isolable. The procedure was the same as the preceding experiment except that (a) the reaction mixture was held under reflux 30 hours (steam-bath), (b) half the amounts of the reactants were used, and (c) the crude product, after removal of thionyl chloride, was flash distilled (bath 197-202°). There were thus obtained (a) 80.8 g. (81%) of TMP,  $n_D^{20}$  1.4831 (lit. 1.4853), b.p. 135-137°, and (b) residue, which when simply distilled gave 11.2 g. (11%) of allyl TMP, b.p. 153.5-157.2°, and undistilled residue, 3.7%.

**Powdered Soft Glass as Catalyst in Allylic Rearrangement of TMP to Allyl TMP.**—A teaspoonful of powdered soft glass was mixed into 193.5 g. of TMP in a 3-necked flask fitted with a reflux condenser, a sealed stirrer, and a thermometer in the liquid and protected from atmospheric moisture. Rapid mechanical stirring was necessary to prevent severe troublesome bumping during reflux. Effective stirring also kept the powdered glass suspended. With refluxing and external heating, the temperature in the liquid gradually rose to 157° at the end of 12 hours. Simple distillation of the liquid (crude allyl TMP) resulted in 3.1 g. of forerun, and 174.3 g. (90%) allyl TMP, b.p. 152-157°.

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### Chemistry of Aliphatic Phosphonic Acids. II. Dielectric Constants and Viscosity of Some Higher Alkylphosphonates

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Several determinations of dipole moments of various trialkyl phosphates can be found in the chemical literature. However, only one set of such determinations in the class of alkylphosphonates exists; this set of values was obtained for a very restricted number of such esters.<sup>1</sup> As a part of a comprehensive study of these compounds we determined the dielectric constants of several diethyl alkylphosphonates, containing an even

(1) A. E. Arbuzov and P. I. Rakov, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim., nauk*, **237** (1950).