acetone used to rinse out the tube. Development by the p-phenylenediamine solution was then carried out in the usual manner. The dye in the eluate could be determined directly without the addition of acid.

The curves obtained with the p-phenylenediamine developer are regular in shape, resembling those of hydroxylamine in Fig. 2. A concentration series was run over a range of 100-fold. The dependence of elution upon concentration of p-phenylenediamine is illustrated in Fig. 4. Here, the logarithm of the maximum slope of the elution curve is plotted against the logarithm of the concentration of the p-phenylenediamine. A straight line of slope of 0.55 was obtained for each dye. If the maximum slope of the elution curve is a measure of the amount of p-phenylenediamine adsorbed, the straight lines in Fig. 4 would show that the adsorption is following the Freundlich isotherm. Similar results were obtained for the displacement of merocyanine dyes.

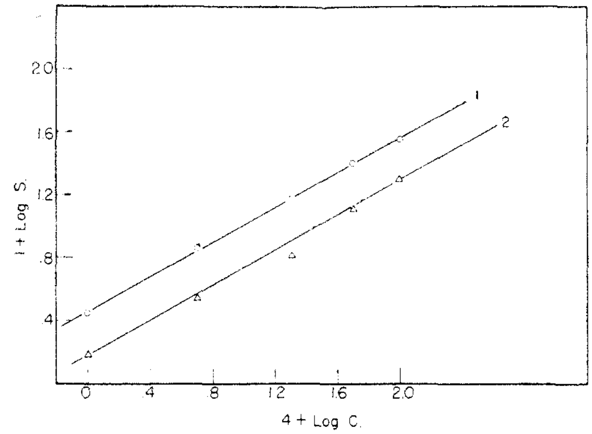

Fig. 4.—Dependence of displacement of dyes upon the concentration of p-phenylenediamine: curve 1, displacement of phenosafranin; curve 2, displacement of 3,3′-diethyloxacarbocyanine.

Some tests were made on the displacement of phenosafranin by 4-amino-3-methyl-N-ethyl-N-(β-methylsulfonamidoethyl)-aniline. The displacement curves obtained are similar in form to those obtained with p-phenylenediamine. The maximum slopes are 1.76 and 0.50 for developer concentrations of 0.01 and 0.001 M, respectively. If these data are plotted in the same way as the p-phenylenediamine data in Fig. 4, the slope of the straight line is 0.54, in excellent agreement with the value of 0.55 for the p-phenylenediamine. It is of interest to compare this concentration-dependence with that found by Fortmiller and James[3] for the development of liquid emulsions by derivatives of p-phenylenediamine. A log–log plot of their data yields a straight line of slope 0.54.

Discussion

The dye displacement experiments have demonstrated that hydroquinone, catechol, hydroxylamine, hydrazine, p-phenylenediamine and 4-amino-3-methyl-N-ethyl-N-(β-methylsulfonamidoethyl)-aniline are adsorbed by silver bromide. This supports the suggestion of Sheppard and Meyer[4] that adsorption of photographic developing agents by silver halide precedes the reduction of the silver salt in photographic development. The pH-dependence of displacement by hydroquinone and catechol indicates that these agents are adsorbed in the ionized form. Kinetic evidence indicates that the ionized forms of the developing agents likewise are involved in photographic development. Resorcinol is much less effective than hydroquinone and catechol, both in displacing the merocyanine dye and in photographic development. The low developer activity of the resorcinol can depend only in part on its lower adsorption, however, since the oxidation of this agent by silver ions from solution is much slower than the oxidation of hydroquinone and catechol.

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[3] L. Fortmiller and T. H. James, *PSA Journal*, **17B**, 102 (1951).

[4] S. E. Sheppard and G. Meyer, THIS JOURNAL, **42**, 689 (1920).

Remarks on Spectra of Stilbene Derivatives

BY JOHN R. PLATT

Application of first-order perturbation theory[1] to the spectra of stilbene derivatives as given by Beale and Roe[2] leads to some important conclusions. For an allowed even–odd transition in a centrally symmetric molecule, such as the longest wave length transition in *trans*-stilbene, the oscillator strength is the square of a transition moment vector, M.[3] A small perturbation by a substituent, a, at a particular position introduces an additional perturbation vector, m_a. The total intensity becomes the square of the vector sum, $M + m_a$. If there is an angle, θ_a, between the vectors, the oscillator strength in suitable units is

$$\begin{aligned} f &= (M + m_a \cos\theta_a)^2 + (m_a \sin\theta_a)^2 \\ &= M^2 + 2Mm_a \cos\theta_a + m_a{}^2 \end{aligned}$$

and the increment is

$$\Delta f = 2Mm_a \cos\theta_a$$

if m_a is relatively small.

For two substituents at opposite positions, the perturbation vectors will be parallel and the intensity increments will add linearly. (For an even–even transition, they would subtract. For a forbidden even–odd, where M is zero, the perturbation vectors would add linearly, but the intensity increments would go up as the square of the vector sum.[4]) For two substituents at any positions, the total intensity increment will be approximately the sum of the independent increments, in this first-order theory, as long as m_a and m_b are small compared to M.

Examination of Beale and Roe's f-values in the light of these remarks leads to the following conclusions.

(1) **The longest wave length singlet–singlet transition in *trans*-stilbene is necessarily even–odd** (in agreement with all theoretical predictions and with the high intensity. Reason: the 4-methylstilbene intensity is greater than that of stilbene; and the 4,4′-dimethyl intensity is greater still (in arithmetic progression) and not less.

(2) **The $N(CH_3)_2$ perturbation is larger than the** methyl (as noted by Beale and Roe) **and in addition it has the same sign.** Reason: the 4,4′-increments for these substituents add, and do not subtract. The same result has been found[5] for these substituents as they affect the benzene 2600 Å. bands; but the $N(CH_3)_2$ group had a relatively larger effect there.

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[1] J. R. Platt, *J. Chem. Phys.*, **19**, 263 (1951).

[2] R. N. Beale and E. M. F. Roe, THIS JOURNAL, **74**, 2302 (1952).

[3] R. S. Mulliken and C. A. Rieke, *Rep. Prog. Phys.*, **8**, 231 (1941).

[4] J. R. Platt, *J. Chem. Phys.*, **19**, 263, 1484 (1951).

[5] J. R. Platt, unpublished.

(3) **The angle θ for position 3 is almost 90°.** Reason: a methyl group in this position produces little change in intensity.

The effect of substituents in the 2-positions, which probably produce steric hindrance, may be treated by the same perturbation theory, as long as the changes in intensity are relatively small. However, the perturbation vectors in this case are no longer necessarily coplanar with the perturbation vectors produced by substituents at other positions.

These general theoretical conclusions support and validate Beale and Roe's important experimental demonstration that *in a strong transition the intensity increments from substituents in particular positions are additive.*

Independent determination of m_a and θ_a at particular positions does not seem feasible for strong transitions (though it can be done for forbidden transitions[6]). If we assume m_a constant for a given substituent at all positions, θ_a can be approximately determined from the intensity increments except for an ambiguity of sign.

I am indebted to Drs. Beale and Roe for showing me their manuscript in advance of publication.

(6) J. R. Platt, "Electronic Structure and Excitation of Polyenes and Porphyrins," Chapter 4, Vol. 3 of "Radiation Biology," Ed., S. Hendricks, McGraw-Hill Book Co., Inc., New York, N. Y., 1952.

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Autocatalyzed Hydrolysis of Sucrose by Acid

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The rate of hydrolysis of sucrose by acid has been the subject of numerous investigations for over a century. Under the usual conditions in a given experiment at constant temperature, the effective concentration of the acid remains unchanged and the reaction is first order with respect to the concentration of the sucrose. We have found the reaction to be autocatalyzed as much as six-fold by a corresponding increase in the acidity under conditions where the increase in acidity on a mole basis corresponds to less than one-tenth per cent. of the sucrose hydrolyzed.

The reactions were carried out in sealed, clean, acid- and alkali-free, Kimble flasks placed in a bath whose temperature was controlled and recorded continuously to ±0.03°. Reaction was stopped by bringing the pH to 6 ± 0.2 by adding a solution of sodium bicarbonate to the reaction mixture in the bath. Loss of water from the reacting mixture or neutralized solution amounted to less than 1% in all cases.

The fraction of the sucrose hydrolyzed was determined in a manner previously described[2] from measurements of the reducing power of the solution toward a carbonate buffered cupritartrate reagent[3] at pH 8.7. The method eliminates any correction for mutarotation of the liberated sugars. The

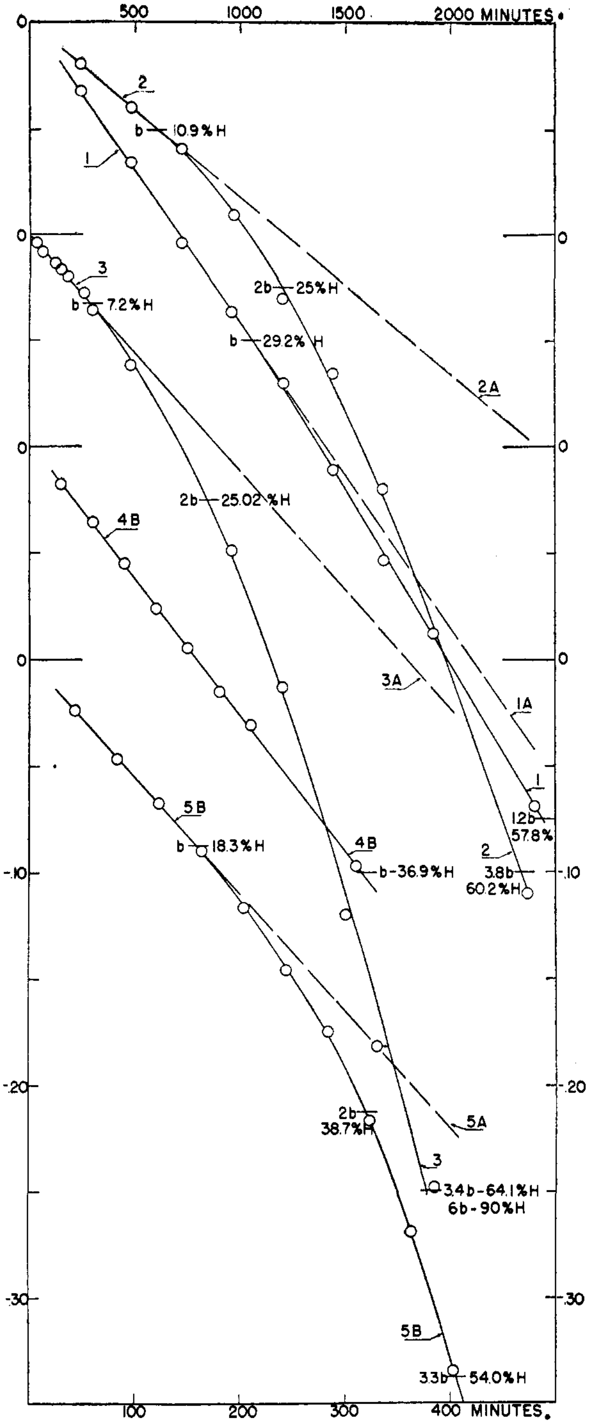

Fig. 1.—Evidence for autocatalysis in the hydrolysis of sucrose by acid. Common logarithms of one minus the fractional hydrolysis of sucrose are plotted as ordinates against the lengths of time the reaction has taken place under the conditions tabulated below. The curves would be straight lines if there were no measurable autocatalysis as is the case for curve 4B. The usual first-order rate constant equals −2.303b. The concentrations given below are the initial formal values at 0° in moles of acid per liter of solution and in g. sucrose (within 1 mg.) in the volume given in ml. (within 0.1 ml.). No color developed in any of the solutions. The % H in the fig. gives the % sucrose hydrolyzed.

Curve	Temp. °C.	10^4(HCl)	Sucrose	Time scale
1	75.10	1.05	2g./100 ml.	Upper
2	75.10	1.05	13g./55 ml.	Upper
3	75.10	2.7	80g./100 ml.	Upper
4B	75.10	5.4	80g./100 ml.	Lower
5B	95.10	1.05	13g./55 ml.	Lower

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[1] The authors are indebted to the Sugar Research Foundation, Inc., for a grant-in-aid.

[2] L. J. Heidt and C. B. Purves, THIS JOURNAL, **66**, 1385 (1944).