[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE COLLEGE]

Spectrophotometric Investigations of Organic Complexes from Copolymerization Monomers: the Instantaneous Complex Formation of Parasubstituted Styrenes and Maleic Anhydride[1]

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RECEIVED APRIL 14, 1953

The formation of highly dissociated 1:1 complexes from para-substituted styrenes and maleic anhydride in benzene is demonstrated. General methods have been applied to indicate the existence of additional complexes when the equilibrium constants are small. Constants which are products of equilibrium constant and molar absorptivities have been evaluated for the prediction of total spectral absorbances of substituted styrene and maleic anhydride mixtures. Styrene and *p*-chlorostyrene show evidences of 2:1 complex formation with maleic anhydride.

It was reported by Bartlett and Nozaki[3] that concentrated mixtures of 1:1 copolymerizing monomers (*e.g.*, stilbene, styrene, etc.) give decided colors when mixed in solution with maleic anhydride. Lewis[4] has compared the relative absorbances of similarly concentrated solutions of substituted styrenes with maleic anhydride using a Corning 511 Filter in a photometer.

Vosburgh and Cooper[5] have developed methods for identification of complexes between compounds that form more than one complex in solution when some special absorption relationships exist. These are based on the continuous variations methods of Job.[6] Hammick and co-workers[7–9] have obtained quantities proportional and, in special cases, equal to the equilibrium constant of such complexes with spectrophotometric techniques when complex stability is low and one complex only is formed.

The purpose of this study was to identify the possible stoichiometric complexes formed by the interaction of maleic anhydride with various parasubstituted styrenes. An increase in absorbance over that expected by Beer's law for 1:1 complexes was observed with an excess of some of the styrenes. The generalized methods presented here for highly dissociated complexes were used to analyze this effect on the premise that the formation of additional complexes accounted for the deviations from Beer's law. Constants were derived on this basis to allow the synthesis of absorption curves for these complexing mixtures at all concentrations and wave lengths.

The complexes of para-substituted styrenes (styrene, *p*-chloro-, *p*-methyl-, *p*-methoxy- and *p*-dimethylaminostyrene) with maleic anhydride in benzene solvent were chosen for study.

Experimental

Materials.—The maleic anhydride (Eastman Kodak Co.) was vacuum distilled at 5 mm. A middle fraction of the distillate, b.p. 90°, was used.

The styrene (Dow Chemical) was vacuum distilled through a 12-inch Vigreux column and a fraction b.p. 41–43° at 14—16 mm., n^{20}D 1.5446, d^{25} 0.907, was used.

All other styrenes were fractionally distilled through a Fenske column 254 mm. long and 10 mm. in diameter with an inner jacket packed with $^1/_{16}''$ glass helices and heated with nichrome wire. The fractionating head was a cold finger type, adapted for collection of small fractions.

The fraction, b.p. 70–72° (4.5–5 mm.), of *p*-chlorostyrene (Monomer–Polymer Co.), n^{20} 1.5643, d^{25}_{4} 1.086, was used.

The fraction of *p*-methylstyrene (American Cyanamid Co.) used was: b.p. 60–70° at 20.5–22 mm., n^{20} 1.5425, d^{25} = 0.889.

The fraction of *p*-dimethylaminostyrene (American Cyanamid Co.) used was: b.p. 104–108° at 4–5 mm., n^{20} 1.6120, d^{25} 0.964.

The *p*-methoxystyrene was prepared in this Laboratory by conversion of 400 g. of *p*-anisaldehyde (Eastman Kodak Co.) to the corresponding substituted cinnamic acid and subsequently decarboxylating by the method of Walling and Wolfstirn.[10]

The benzene (Merck Co. thiophene-free) was distilled immediately prior to use. A middle fraction of the distillate was used in the preparation of solutions.

Benzene solutions of weighed monomers were made up in volumetric flasks maintained at 25 ± 0.03°.

Spectrophotometric Studies.[11]—Spectrophotometric studies were conducted on the complexing mixtures under nitrogen and oxygen without differences in results. No changes in optical density with time were observed with the *p*-methyl-, *p*-chloro- and styrene complexes of maleic anhydride for over three weeks time. Exposure of the mixtures to ultraviolet light for three hours had no measurable effect on the absorbances. The styrenes had no interfering absorptions at the wave lengths studied. The molar absorptivities for maleic anhydride at 5 mμ intervals from 370 mμ through 320 mμ are: 0.030, 0.085, 0.240, 0.760, 1.64, 3.63, 5.94, 9.29, 15.00, 24.50, 33.90. Anhydride absorbance was subtracted from the total observed to obtain the net absorption due to the complexes with the styrenes.

All absorbance readings below 450 mμ were in covered fused silica cells with a Model DU Beckman spectrophotometer at room temperature. Readings above 450 mμ were made in covered Corex cells with a Model B Beckman spectrophotometer.

The Methods of Continuous Variations.—The continuous variations method of Job[6] necessitates the mixing of a styrene solution and a maleic anhydride solution in various ratios. The maleic anhydride solution is a fraction (x) of the total volume of the mixture. The absorbances, A, less the absorbances that can be attributed to the components are plotted against these fractions (x). Figure 1 for maleic anhydride with styrene is typical of the many that were made at various wave lengths for maleic anhydride with styrene, with *p*-chlorostyrene and with *p*-methylstyrene. The solid line segments drawn are based on calculated values described later.

The continuous variations of equimolar solutions of maleic anhydride and all three of these styrenes produced maxima at x = 0.5 which are indicative of 1:1 complexes.[6] These complexes were instantaneously formed. The continuous

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(1) Presented in part at the Fall meeting, 1950, of the American Chemical Society at Chicago, Illinois.

(2) The Upjohn Co. Kalamazoo, Mich.

(3) P. D. Bartlett and K. Nozaki, THIS JOURNAL, **68**, 1495 (1946).

F. F. M. Lewis, in C. Walling, E. R. Briggs, K. B. Wolfstirn and
(4) Mayo, *ibid.*, **70**, 1537 (1948.)

(5) W. C. Vosburgh and G. R. Cooper, *ibid.*, **63**, 437 (1941).

(6) P. Job, *Ann. chim.* [10] **9**, 113 (1928).

(7) D. L. Hammick and R. B. Williams, *J. Chem. Soc.*, 1856 (1935).

(8) D. L. Hammick and R. P. Young, *ibid.*, 1463 (1936).

(9) B. R. Hamilton and D. L. Hammick, *ibid.*, 1350 (1938).

(10) C. Walling and K. B. Wolfstirn, THIS JOURNAL, **69**, 852 (1947).

(11) All spectrophotometric terms, definitions and symbols used in this paper are as in "Suggested Nomenclature in Applied Spectroscopy," H. K. Hughes, *Anal. Chem.*, **24**, 1349 (1952).

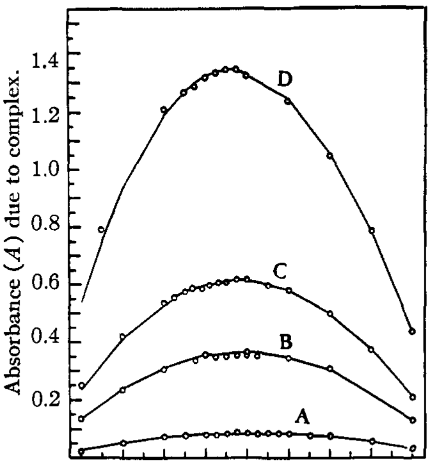

Fig. 1.—Continuous variations of benzene solutions of maleic anhydride and styrene at 360 mμ. Plot of absorbance (A) values against the volume fraction (x) of the maleic anhydride solution in the mixture. The solid lines were calculated from evaluated constants. The molarities of the solutions before mixing were:

Curve	Anhydride soln., M	Styrene soln., M
A	0.250	0.250
B	.133	2.000
C	.100	4.273
D	.100	8.7 (pure styrene)

variations of non-equimolar solutions of these three styrenes with maleic anhydride provided no significant shift in the maxima. This indicates that the 1:1 complexes are highly dissociated. The presence of more highly dissociated complexes is not proven or disproven.

The absorbances of solution mixtures of maleic anhydride with *p*-methoxystyrene and with *p*-dimethylaminostyrene changed with time and the initial values due to the instantaneously formed complexes had to be estimated by extrapolation to zero time. This was difficult to do with high accuracy, especially in the case of *p*-methoxystyrene. However, the instantaneous formation of a red-orange 1:1 complex is shown in Fig. 2 for variations of equimolar solutions of *p*-dimethylaminostyrene and maleic anhydride. An initial 1:1 complex was strongly but not conclusively indicated in the case with *p*-methoxystyrene.

Zero time values from the continuous variations of non-equimolar solutions of *p*-dimethylaminostyrene and maleic anhydride showed shifts in maxima from 0.50 in the directions appropriate[6] for an unique 1:1 complex.

The Job equation

$$K = (p - 1)(1 - 2x_{\mathrm{m}}) \div [\mathrm{S_i}][(1 + p)x_{\mathrm{m}} - 1]^2 \quad (1)$$

is insensitive for the determination of small equilibrium constants by continuous variations of non-equimolar solutions. Even such extreme values of the parameters as when S_i, the molar concentration of the *p*-dimethylaminostyrene solution, is 0.05; p, the ratio of the maleic anhydride solution molarity to the *p*-dimethylaminostyrene molarity before mixing, is 20.0; shift the value, x_{m}, at the maximum of the curve only 0.05 ± 0.03 unit to 0.45. As measured at 500 mμ this equilibrium constant of the 1:1 complex is about 0.5. With the other styrene complexes the probable error of the method was greater than the equilibrium constants.

Discussion

Other highly dissociated complexes may be formed with significant absorption at the wave lengths studied. Space limitations only permit outlining of the methods used in the analysis.

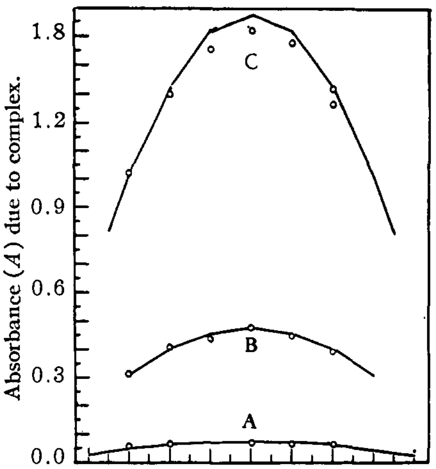

Fig. 2.—Continuous variations of equimolar solutions of maleic anhydride (0.250 M) and *p*-dimethylaminostyrene (0.250 M). Plot of instantaneous values of absorbance (A) against the volume fraction (x) of the maleic anhydride solution in the mixture. The solid lines were calculated from evaluated constants. The curves were measured at different wave lengths: A, 600 mμ; B, 550 mμ; C, 500 mμ.

The equilibria for the complexes may be formulated

$$S + M \rightleftharpoons C_1 = SM\,(K_1 = \text{equilibrium constant}) \quad (2)$$

$$C_1 + (n - 1)\,S + (m - 1)\,M \rightleftharpoons C_2 = S_{\mathrm{n}}M_{\mathrm{m}}\,(K_2 = \text{equilibrium constant}) \quad (3)$$

For highly dissociated complexes where S and M are the molar concentrations of the styrene and maleic anhydride, respectively, the total absorbance, A_{t}, may be written as the sum of the absorbances of both complexes, where C_1 and C_2 are concentrations and ϵ_1 and ϵ_2 are their respective molar absorptivities.

$$A_{\mathrm{t}} = \epsilon_1 C_1 + \epsilon_2 C_2 = \epsilon_1 K_1 SM + \epsilon_2 K_1 K_2 S^n M^m \quad (4)$$

At constant M

$$(\partial A_{\mathrm{t}}/\partial S)_{\mathrm{M}} = \epsilon_1 K_1 M + n\epsilon_2 K_1 K_2 S^{n-1} M^m \quad (5)$$

From the plot of A_{t} *vs.* S the values of $\partial A_{\mathrm{t}}/\partial S$ at various S were obtained as the instantaneous slopes. Plots of these slopes at their respective S values gave a second slope corresponding to

$$(\partial^2 A_{\mathrm{t}}/\partial S^2)_{\mathrm{M}} = n(n - 1)\epsilon_2 K_1 K_2 S^{n-2} M^m \quad (6)$$

The extrapolated intercept gave the value of $\epsilon_1 K_1 M$.

It was observed by this method in the *p*-chlorostyrene and styrene mixtures with maleic anhydride that $n = 2$ and thus this second slope was a constant of value $2\epsilon_2 K_1 K_2 M^m$. For various trials, each at constant M values, m and the other constants were evaluated. In the cases studied $m = 1$ and it may be assumed that the 1:1 complex does not dimerize. The nearest integral values of $(n - 2)$ in the general case were also simply determined by a log–log plot of the second slopes at their S instantaneous values as

$$\log\,(\partial^2 A_{\mathrm{t}}/\partial S^2)_{\mathrm{M}} = (n - 2)\log S + \log n(n - 1)\epsilon_2 K_1 K_2 M^m \quad (7)$$

The values observed were $m = 1$ and $n = 2$. Equation (4) may then be reduced to

$$A_t/MS = \epsilon_1K_1 + \epsilon_2K_1K_2S \qquad (8)$$

A plot of the quotient, total absorbance of complexes (A_t) divided by the product of the molar concentrations of the reactants, *e.g.*, *MS*, against one widely varying reactant concentration, *e.g.*, *S*, at low concentration values of the other, *M*, should give a straight line of positive slope if there is further interaction of this nature with styrenes; of zero or negative slope if there is only one complex. Figures 3 and 4 represent such plots for the styrene and *p*-chlorostyrene complexes with maleic anhydride. This demonstrates an increase in absorbance over that expected by Beer's law for a 1:1 complex and may be explained by the further interaction of 1:1 complexes with these styrenes.

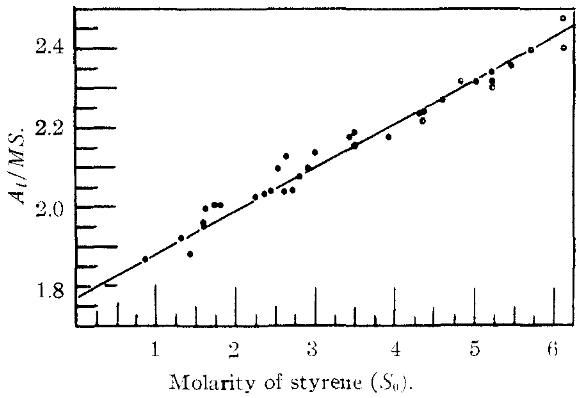

Fig. 3.—Plot of the quotient, absorbance (A) divided by the product of the maleic anhydride concentration (M) and the styrene concentration (S) against the molarity of the styrene at 370 mμ.

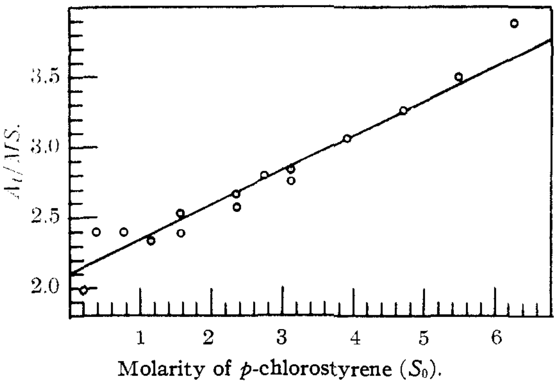

Fig. 4.—Plot of the quotient, absorbance (A) divided by the product of the maleic anhydride concentration (M) and the *p*-chlorostyrene concentration (S) against the molarity of the *p*-chlorostyrene at 375 mμ.

The ϵ_1K_1 and $\epsilon_2K_1K_2$ values are determined from the slope and intercept of such plots.

No such further interaction of the instantaneous 1:1 complex of maleic anhydride with *p*-methylstyrene, *p*-methoxystyrene and *p*-dimethylaminostyrene was observed. The ϵ_1K_1 values of these complexes were obtained from the plots of their absorbances against styrene molarities for constant maleic anhydride molarity. Since $m = n = 1$ in these cases, ϵ_1K_1 is the linear slope as per equation (5).

The evaluated constants, ϵ_1K_1 and $\epsilon_2K_1K_2$, are given in the graph of their logarithms against wave lengths in mμ (Fig. 5). These constants were used in equation (4) to calculate the complex absorbances denoted by the solid lines in Figs. 1 and 2.

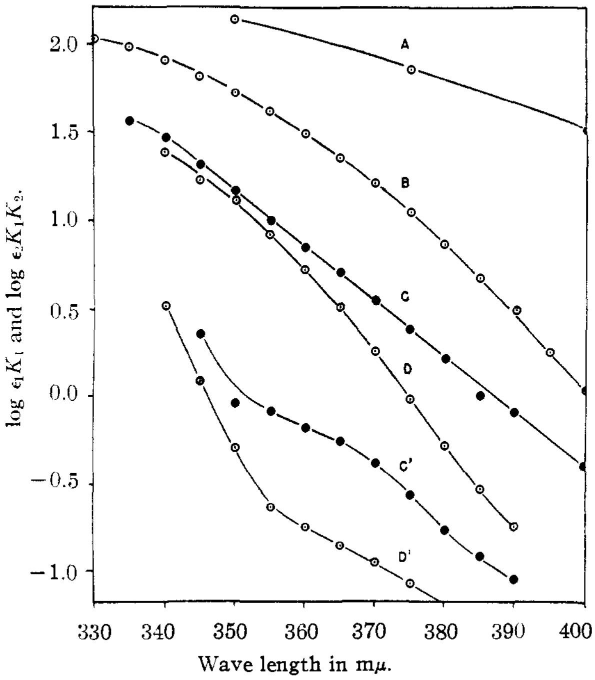

Fig. 5.—The logarithm of products of molar absorptivities (ϵ) and equilibrium constants (K) of complex formation are plotted at various wave lengths in mμ. Curves A, B, C and D are for the instantaneously formed 1:1 complexes of maleic anhydride with *p*-methoxystyrene, *p*-methylstyrene, *p*-chlorostyrene and styrene, respectively; log ϵ_1K_1 *vs.* mμ. Curves C′ and D′ are for the possible 1:2 complexes of maleic anhydride with *p*-chlorostyrene and styrene, respectively; log $\epsilon_2K_1K_2$ *vs.* mμ. The log ϵ_1K_1 values for the instantaneously formed 1:1 complex of maleic anhydride with *p*-dimethylaminostyrene are 2.44 at 360 mμ and 2.42 at 365 and 375 mμ. At 50 mμ intervals starting with 400 mμ through 650 mμ the log ϵ_1K_1 values are: 2.37, 2.29, 2.00, 1.48, 0.68, 0.30.

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