ORGANIC COMPLEXES FROM COPOLYMERIZATION MONOMERS PARA SUBSTITUTED STYRENES AND MALEIC ANHYDRIDE

Thesis for the Degree of Ph. D. MICHIGAN STATE COLLEGE Edward Robert Garrett 1950

This is to certify that the

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"Organic Complexes from Copolymerization Monomers: Para Substituted Styrenes and Maleic Anhydride'

presented by

Edward R. Garrett

has been accepted towards fulfillment of the requirements for

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ORGANIC COMPLEXES FROM COPOLYMERIZATION MONOMERS: PARA SUBSTITUTED STYRENES AND MALEIC ANHYDRIDE

Ву

EDWARD ROBERT GARRETT

A THESIS

Submitted to the School of Graduate Studies of Michigan State College of Agriculture and Applied Science in partial fulfillment of the requirements for the degree of

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Department of Chemistry

1950

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The writer wishes to express his appreciation to Dr. Ralph L. Guile for his counsel and guidance.

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DEDICATION

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To my wife, her patience and cooperation

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INTRODUCTION

Complex formation in solution can be investigated by studies of the change in physical properties of the solution. Macro properties, such as boiling point and freezing point changes, viscosity variations etc. have the disadvantages of not showing detectable variations when the amount of complex formed is extremely small. Spectra, however, afford an additive property that allows for the detection of small concentrations.

Color formation has been noted in solutions of monomers that tend to copolymerize in alternate fashion. No exact quantitative study has yet been made on light absorption, the equilibrium constants (if any) and the exact composition of the complexes between such monomers when they are modified by different substituent groups. Such a study may add to the understanding of the transition state between attacking radicals and monomers in the alternating type copolymerization.

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HISTORICAL AND THEORETICAL BACKGROUND

1. Colored Complexes in Solution.

The fermation of "molecular compounds" or "complexes" in solution that develop color is a well known phenomenon. Particular examples are the Wurster salts, quinhydrone structures^{1,2,3}, hydrocarbon-pierate addition compounds and hydrocarbon-tetranitro methane complexes^{4,5,6}. Maatman, in a recent study⁶ on the color forming properties in solution, has made a rather complete survey of existent theories and listed an extensive bibliography. These have also been considered in part by Wheland³. The plausible theories of interaction to form molecular compounds have been classified as to covalent, ionic and polarization theories.

In his discussion of the relative validity of these theories, Maatman⁶ states that the covalent theory^{7,8,9} appears invalid as bond energies greater than those obtained for molecular compounds are generally associated with covalence. (The high eptical extinction values of such complexes for small concentrations tend to confirm this.) He dismisses the ionic theory 10,11 on the premise that it is extreme to postulate a complete transfer of electrons from donor to acceptor melecules in non-ionizing solvents and that existent experimental data could also confirm a polarization hypothesis. Maatman contends that a polarization theory 5,12,13,14based en specific interactions between pairs of molecules is unwarranted when true equilibrium exists and

-2-

postulates a "pelarization aggregate" to explain low interaction energy and color formation by stabilization of resonance contributions¹⁴. A mechanistic picture of this aggregate is not presented and the postulate is not further clarified. Woodward²⁰ has attempted to correlate a polarization aggregate concept with Weiss' ionic theory of electron transfer¹⁰.

Maatman also states that no absorption peaks characteristic of the molecular compound have been observed indicating merely a shift of the absorption to the red and no apparent correlation between the shift and the complex's stability.

2. Alternating Type Copolymerization and the Formation of Colored Complexes.

In the last decade, the copolymerization problem has been studied extensively by Mayo et al and has been the subject of a thorough review¹⁵. The experimental approach^{16,17} involved the determination of the relative reactivity of a copolymerizing radical with a like and an unlike monomer based on the elementary analysis of the composition of the copolymer after a noted interval of copolymerization. On the basis of this treatment an attempt has been made to fit random type copolymers (e.g. styrene - butadiene) and alternating type copolymers (e.g. styrene - maleic anhydride) into an overall kinetic picture and to provide a quantitative estimate of the effect of substituents on monomer attack by free radicals ¹⁸⁻²³. In the course of this work, special

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attention was placed on the alternating or 1:1 copolymerizing properties of certain monomers.

Bartlett and Nezacki²⁴ did not discover any characteristic abnormalities in vapor pressures, mutual solubilities and viscosities of mixtures of monomers showing tendency toward 1:1 copolymerization altho concentrated mixtures of such monomers as stilbene, styrene, 1,1 diphenyl ethylene gave decided colors when mixed in solution with maleic anhydride. They suggested that resonant structures and polarities may allow the monomers to act as electron donors and acceptors respectively. Thus polar chromophoric intermediates may occur that facilitate the alternating tendencies in the copolymer.

Mayo et al¹⁹⁻²², on the basis of the relative reactivity ratios of monomers in copolymerization, state that a relation exists between the relative reactivity of a monomer, independent of the attacking radical, and the tendency of substituents on the olefinic carbons of the monomer to accept electrons from the double bond. Relative reactivity is a measure of the rate of radical attack on the unlike or other monomer in ratio to its attack on the monomer from which it is furnished. However, monomers that are of the alternating type show anomalous divergence from this series.

Walling et al²² attempted to apply the Hammett relation²⁵: $\log K_0/K = \sqrt{2}$ where K_0 and K are the rates or equilibrium constants for the reaction of the unsubstituted and substituted compound respectively,

 ∇ a parameter having a single value for each ortho, meta or para aryl substituent and \bigcirc a constant for

-4-

any particular reaction. The parameter ${\bf \nabla}$ is a measure of the ability of a substituent to withdraw or make available electrons at the site of the reaction: /? 13 a measure of such electron availability on the reaction considered. Copolymerizations of a series of substituted styrenes with selected monomers were carried out and relative reactivity of the various styrenes toward the radical was calculated. A plot of the log of the relative reactivity against the Hammett ∇ value should be linear. This is true with the unsubstituted styrene radical but with radicals derived from methyl methacrylate and maleic anhydride there is no consistent relation. Para methyl, para methoxy and para dimethyl amino styrenes have exceedingly high relative reactivities toward maleic anhydride but conform to the Hammett linear principle in being less reactive toward styrene than electron acceptor substituents.

Mayo and Walling^{15,21} have attempted to explain this apparent anomaly: namely that relative reactivities show the poorest correlation with polar reactions (alternating copolymerization) where polar phenomena should be most important, by proposing that "the major driving force for strong alternation tendencies is not simple polarization, but arises from contributions to the transition state of forms in which actual electron transfer between radical and monomer (or vice versa) has taken place". In the case of addition of styrene radical (electron donor) to maleic anhydride, transition structures such as these could be involved:

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In the conjugate reaction of anhydride radical (electron acceptor) with monomeric styrene the contributing structures of an anhydridecarbanion (or relatively stabilized enclate ion) and a benzyl carbonium ion could be constructed. Thus resonance stabilization of the activated complex may account for the observed alternating tendencies. This interpretation also explains the increased alternating effects of p methyl, p methoxy and p dimethylamino groups on the styrene as a greater number of additional resonance structures becomes available on such substitution:



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Qualitative correlation between the tendency of substituents to influence alternation and the intensity and wave length of the color absorption of molecular complexes²¹ showed the similarity in structures of molecular compounds and the activated complexes of alternating copolymerization 15,23. Om the assumptions of a 1:1 complex and complex stability being propertional to optical density, the relative absorption of similarly concentrated solutions of substituted styrenes with maleic anhydride, trinitrobenzene and chloranil were compared in a photometer using a Corning 511 filter (transmission range: approximately 350 m µ to 480 m µ ; maximum transmission at 410 m μ). A radical-ion structure based on the concepts of Weiss¹⁰ was postulated for the complex in which an electron has been donated by the hydrocarbon to the carbonyl derivative: 23,26

$$\begin{array}{c|c} \mathbf{H}\mathbf{C} & -\mathbf{C}\mathbf{H}_2 \\ \hline & & & \\ & &$$

The possibility of alternation proceeding thru the addition of 1:1 complexes to a growing chain is deemed improbable by Mayo et $al^{15,23}$ on -7-

the following bases:

(a) Dilution has small effect on the copolymerization²⁷ whereas if true equilibrium exists, the effect on molecular complexes would be large.

(b) There are no evidences of physical 21,23 association.

(c) There is no change in monomer reactivity ratios on dilution. 21,27,28

(d) There is no unequivocal kinetic evidence in alternating systems.¹⁵

Mayo and Walling¹⁵ conclude that "growth of copolymers by addition of molecular complexes could either be excluded or could not be demonstrated in any of a number of strongly alternating systems. Similar interaction between radicals and monomers, however, accounts for alternation tendencies."

The arguments against alternating type copolymerization depending directly on complex formation are based on the following premises:

(a) A 1:1 complex is formed.

(b) The molecular complex obeys the laws of true equilibrium and thus is affected by dilution.

(c) It is intimated^{15,21,23} that the observed optical density of similarly concentrated solutions of substituted styrenes and a conjugated carbonyl derivative at one absorption band is proportional to the stability of the formed complex.

(a) and (b) have not been experimentally proven.
(c) is not warranted on the basis of prior spectrophotometric investigations of colored complexes⁶. 3. The Method of Continuous Variations.

The method of continuous variations was originally developed by P. Job²⁹ to determine the composition of complexes in solution and their stability. The following mathematical development is largely based on his work.

Complex formation may be symbolized by an equilibrium:

(1) mA + nB \rightarrow A_mB_n

Let a solution, (a), be [A] molar in A molecules and a solution, (b), be [B] = p [A] molar in B molecules. The method of continuous variations involves mixing varying volumes of (a) and (b) and measuring a property (P) of these mixtures. Let 1-x be the fraction (a) of the total volume of the final mixture while x is the fraction of (b) assuming no contraction or expansion on mixing.

The development of appropriate relations between a property (P) and the volume fraction (x) is based on finding the value of x for which the concentration of the complex is a maximum.

The mass action law may be expressed:

(2) $|A|^m \times |B|^n = K |A_m B_n|$

The total number of moles of A in the (a) fraction is partly combined in the complex after equilibrium is attained. This amount is given by:

(3) $|A|_0$ (1-x) = $|A| + m |A_m B_n|$

Similarly, for the number of moles of B:

(4) $|B|_0 \mathbf{x} = p |A|_0 \mathbf{x} = |B| + n |A_m B_n|$

Taking the derivatives of (2), (3) and (4) with respect to x:

(2')
$$\underset{m \mid A \mid}{}^{m-1} \mid B \mid n \quad \frac{d \mid A \mid}{dx} + n \mid B \mid n-1 \mid A \mid m \quad \frac{d \mid B \mid}{dx} =$$

$$K \frac{d |A_m B_n|}{dx}$$
(3!) - |A| = $\frac{d |A|}{dx} + m \frac{d |A_m B_n|}{dx}$

(4')
$$p|A|_0 = \frac{d|B|}{dx} + n \frac{d|A_mB_n|}{dx}$$

To determine the conditions under which a maximum (or minimum) of complex exists, let $\frac{d|A_mB_n|}{dx} = 0 \quad \text{and then (2!) becomes:}$

(5)
$$m |A|^{m-1} |B|^n \frac{d |A|}{dx} + n |B|^{n-1} |A|^m \frac{d |B|}{dx} = 0$$

$$\frac{dx}{dx}$$

Dividing thru by |A| m-1 |B| n-1,

(6)
$$m|B|\frac{d|A|}{dx} + n|A|\frac{d|B|}{dx} = 0$$

(3') becomes:

$$\frac{d IAI}{dx} = -IAI_0$$

(4') becomes:

$$\frac{d |B|}{dx} = p |A|_{0}$$

Substituting (7) and (8) in (6) gives:

$$(9) - m|B| |A|_0 + n|A| p|A|_0 = 0$$

 $(10) |B| = \frac{np}{m} |A|$

and substituting (10) in (2):

(11)
$$\left(\frac{np}{m}\right)^n |A|^{m+n} = K |A_m B_n|$$

and substituting (10) in (4):

(12)
$$p|A|_0 x = \frac{np}{m}|A| + n|A_mB_n|$$

where

(13)
$$|A_m B_n| = \frac{p}{n} |A|_0 = \frac{p}{m} |A|$$

From (3), also:

(14)
$$|A_m B_n| = \frac{|A|_0 (1-x) - |A|}{m}$$

Equating (13) and (14) and simplifying:

(15)
$$|A| = |A|_0 \frac{(n+mp) \times -n}{n(p-1)}$$

and from (3):

(16)
$$|A| = |A|_0 (1-x) - m |A_m B_n|$$

whereas from (13):

$$(17) |A| = \frac{m}{n} |A|_0 \mathbf{x} - \frac{m}{p} |A_m B_n|$$

Equating (16) and (17), simplifying and solving for eoneentration of complex:

(18)
$$|A_m B_n| = p |A|_o \frac{n - x(n+m)}{nmp - nm} = p |A|_o \frac{n - x(n+m)}{nm(p-1)}$$

.

Substituting (15) and (18) in (11) gives:

(19)
$$\left(\frac{np}{m}\right)^n |A|_0^{m+n} \left\{\frac{(n+mp)_{x-n}}{n(p-1)}\right\} = Kp |A|_0 \frac{n-x(n+m)}{nm (p-1)}$$

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Simplifying:

$$(20) \frac{|A|_{m+n-l_{p}n-l_{(n+mp)x-n}}^{m+n-l_{m+n-l_{(n+mp)x-n}}} = K\{n-x(n+m)\}$$

or:

$$\frac{(21)}{m^{n-1}n^{m-1}(p-1)} \frac{(n+mp)x-n}{(n+mp)x-n} = K$$

Equation 21 is satisfied by values of x for which the concentration of the complex $|A_m B_n|$ is a maximum (or minimum).

It can be seen from equation (20) that the equilibrium constant need not be specified only if

(22) (n+mp)x-n = 0 and thus

(23) $n-x(n+m) \equiv 0$ and thus

(24) $x = \frac{n}{n+mp} = \frac{n}{n+m}$ from which it is apparent that

(25) p = 1

Thus the necessary condition for the value of x to correspond to the proportions of the two constituents that react to form the complex is that the molar concentrations of solutions (a) and (b) be equal. Knowing the formula of the complex $A_m B_n$ and x for the greatest complex concentration, the equilibrium constant can be evaluated using equation (21).

Since the complex concentration cannot be directly measured in solution, a variation in a property (P) of the mixture is studied as a function of the mixture's composition. P is a function of the concentrations of the constituents and the complex

(26) $P = f(|A|, |B|, |A_m B_n|)$

If the concentrations of the two solutions (a) and (b) are fixed P depends only on x. On variation of the volumes of the two solutions, i.e. (x) and (1-x), P will have a maximum (or minimum) dependent on the extent of reaction between A and B molecules. To determine the relationship of the variables on the attainment of this property maximum, differentiate the function (26) with respect to x and maximize by equating to zero.

$$(27) \quad \frac{dP}{dx} = \frac{\partial f}{\partial x} = \frac{\partial f}{\partial |A|} + \frac{\partial f}{\partial |x|} + \frac{\partial f}{\partial |B|} + \frac{\partial f}{\partial |A|} + \frac{\partial f}{\partial |A|} = 0$$

The necessary postulate is that the property is a maximum (or minimum) for the maximum concentration of the complex i.e.:

$$\begin{array}{c} (28) \quad \frac{d}{dx} \left[A_m B_n \right] = 0 \\ dx \end{array}$$

Substituting (7) and (8) in (27) realizing (28) in (3°) and (4°) :

(29)
$$-\frac{1}{2}\frac{1}{|A|}$$
 $|A|_{0} + \frac{1}{2}\frac{1}{|B|}$ p $|A|_{0} = 0$

<u>Case (a):</u> If P is a maximum only when the concentration of the complex is a maximum it follows that, in general, the function is independent of the equilibrium concentrations of the constituents (i.e. |A| and |B|) and so

$$\begin{array}{c} (30) \quad \underline{35} \\ \underline{3|A|} \quad \underline{35} \\ \underline{3|B|} \quad \underline{0} \end{array}$$

Thus the property is a maximum when the complex concentration is a maximum. Using a spectrophotometric property, this case is applicable when the reactants show no absorption at the wave length used. If the complex alone absorbs, then the maximum optical density (D) corresponds to the maximum in P and the maximum in complex concentration. The corresponding volume fraction gives the requisite value of x.

<u>Case (b):</u> If the property is dependent on the concentrations of the reactants (e.g. both A and B molecules absorb at the specific wave length used in a spectrophotometric method) no interaction between complex and reactants is postulated. If the property studied is additive then, letting Y be the difference between the value of the property observed for the reactants plus complex and for the initial constituents assuming no reaction; it follows from (26)

(31) $Y = f(|A|, |B|, |A_mB_n|) - f(|A|_0(1-x), 0, 0) - f(0, |B|_{OX}, 0)$ This Y difference is maximized by differentiating (31) with respect to x and equating to zero:

$$(32) \frac{\partial Y}{\partial x} = \frac{\partial f}{\partial |A|} \frac{\partial |A|}{\partial x} + \frac{\partial f}{\partial |B|} \frac{\partial |B|}{\partial x} + \frac{\partial f}{\partial |A_m B_n|} \frac{\partial |A_m B_n|}{\partial x} = \frac{\partial |A_m B_n|}{\partial x} = \frac{\partial |A_m B_n|}{\partial |A| o x} + \frac{\partial |A_m B_n|}{\partial |A| o x} + \frac{\partial |A_m B_n|}{\partial |A| o x} = \frac{\partial |A_m B_n|}{\partial x} = \frac{\partial |A_m B_n|}{\partial |A| o x} + \frac{\partial |A_m B_n|}{\partial |A| o x} + \frac{\partial |A_m B_n|}{\partial |A| o x} + \frac{\partial |A_m B_n|}{\partial |A| o x} = \frac{\partial |A_m B_n|}{\partial |A| o x} + \frac{\partial |A| o x}{\partial |A| o x} + \frac$$

0

Substituting (7) and (8) in (32) and completing the differentiation:

$$(33) - |A|_{0} \frac{\partial f}{\partial |A|} + p |A|_{0} \frac{\partial f}{\partial |B|} + \frac{\partial f}{\partial |A_{m}B_{n}|} \frac{\partial |A_{m}B_{n}|}{\partial x} + |A|_{0} \frac{\partial f}{\partial |A|_{0}(1-x)}$$

$$- p |A|_{0} \frac{\partial f}{\partial \{p |A|_{0}x\}} = 0$$

(28) is the condition to specify for the property difference (Y) to be a maximum when complex concentration is a maximum and (33) becomes: (34)

$$-|A| \circ \left(\frac{\partial f}{\partial |A|} - \frac{\partial f}{\partial |A|}\right) + p |A| \circ \left(\frac{\partial f}{\partial |B|} - \frac{\partial f}{\partial |B|}\right) = 0$$

This equation (34) was derived considering the additivity of the contributions from A, B and A_mB_n to the property (P) (i.e. we consider Beer's law to hold in the spectrophotometric method). Thus the rate of change of the property (P) with respect to any change in the concentration of A and B is constant:

 $(35a) \qquad \underline{\partial f} = \text{constant} = a$

$$(35b) \qquad \underline{\partial f} = constant = b$$

and substituting (35a) and (35b) into (27):

(36)
$$\frac{dP}{dx} = a \frac{\partial |A|}{\partial x} + b \frac{\partial |B|}{\partial x} + \frac{\partial f}{\partial |A_m B_n|} \frac{\partial |A_m B_n|}{\partial x}$$

which integrates to:

(37)
$$P = a |A|+b |B| \frac{\int f}{\int |A_m B_n|} |A_m B_n|$$

where the last term is some function of the complex concentration ($\phi |A_m B_n|$). Thus, in effect, as per equation (31) the Y curve is only a plot of some function of the complex concentration.

To summarize the method of continuous variations when only one complex is formed:

1. The mixtures of equimolar solutions of (a) and (b) are varied to determine the formula of the complex.

2. The mixtures of non-equimolar solutions of (a) and (b) are varied to determine the equilibrium constant of the complex.

Three cases exist:

<u>Case (a)</u>: The measured property is independent of the equilibrium concentrations of the two reastants and depends only on concentration of the complex. The curve of property (P) value against mixture composition (x) passes thru a maximum or minimum for the maximum concentration of the complex alone. <u>Case (b)</u>: The measured property is an additive function of concentrations of the complex and the reactants. The curve of the difference (Y) between the experimental values and those that would have been observed if no complex formation had occurred is constructed against the mixture composition (x). This can easily be cone by plotting the difference in the experimentally observed values and the values from a straight line joining the points given by the individual reactants. This curve of difference (Y) gives a maximum or minimum for the maximum concentration of the complex.

<u>Case (c):</u> If the measured property depends on some complicated relation of the constituents present in a mixture, the variational study does not permit the determination of maximum complex concentration.

The method as outlined can be applied directly only if:

1. the two reactants have a well determined molecular formula and there is no dimerization, etc.

2. the complex is unique, i.e. only one species exists.

3. the law of mass action is applicable.

Experimental verification of these facts can be obtained by the determined complex formula being the same for all limits of concentration; no matter how dilute the solutions of equimolar mixtures. For all non-equimolar mixtures the obtained value of the equilibrium constant is a constant for highly divergent conditions.

Vosburgh and Cooper³⁰ developed relations to specifically apply the spectrophotometric method. Consider the Beer-Lambert Law:

(38) $I = I_0 10^{-EC1}$

where: I I the intensity of light transmitted.

 I_0 is the initial light intensity.

E is the specific extinction or extinction coefficient per unit concentration per cm of absorption cell length.

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C is the concentration

l is the absorption cell length.
From (38) we get the logarithmic expression:
(39)

$$D = \log \frac{I_0}{I} = EC1$$

where D is defined as the optical density. Let E_1 , E_2 , E_3 be the extinction coefficients of A, B and $A_m B_n$ at a wave length (λ). Then the optical density (D) is the measured property (P):

 $(40) D = \mathcal{L}(E_1 |A|+E_2 |B|+E_3 |A_mB_n|)$

Letting Y be the difference between the density of (40) and the density of the solution if there had been no complex formation:

(41)

 $Y = \int (E_1 |A| + E_2 |B| + E_3 |A_m B_n| - E_1 |A|_0 (1-x) - E_2 px |A|_0)$ Differentiating (41) with respect to x and maximizing: (42)

$$\frac{dY}{dx} = \int (E_1 \frac{d|A|}{dx} + E_2 \frac{d|B|}{dx} + E_3 \frac{d|A_mB_n|}{dx}$$

 $+ E_1 |A|_0 - E_2 p|A|_0 = 0$

Substituting equations (3') and (4'):

$$(43) = E_1 \left(-m \frac{d|A_m B_n|}{dx} - |A|_0 \right) + E_2 \left(-n \frac{d|A_m B_n|}{dx} + p|A|_0 \right)$$

+
$$E_3 \frac{d|A_mB_n|}{dx}$$
 + $E_1|A|_0 - E_2 p|A|_0 = C$

which on simplifying becomes:

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(44)
$$\frac{d|A_m B_n|}{dx} \left(-mE_1 - nE_2 + E_3\right) = 0$$

which is generally true when

$$\frac{d/A_mB_n}{dx} = 0$$

i.e. Y is maximum or minimum when the concentration of the complex is a maximum.

If $E_3 > (m E_1 + n E_2)$, Y is a maximum. If $(m E_1 + n E_2) > E_3$, Y is a minimum.

Vosburgh and Cooper also investigated the relations when two complexes are formed, the second in the manner:

(46) $A_m B_n + qB \leftrightarrow A_m B_{n+q}$

then

(47)
$$Y = \mathcal{L}(E_1 | A | + E_2 | B | + E_3 | A_m B_n | + E_4 | A_m B_{n+q} |$$

- $E_1 | A |_0 (1-x) - E_2 | A |_0 px$)

Maximizing and simplifying as before:

(48)

$$\frac{dY}{dx} = \int \left(\mathbf{E}_1 \frac{d|\mathbf{A}|}{dx} + \mathbf{E}_2 \frac{d\mathbf{B}}{dx} + \mathbf{E}_3 \frac{d|\mathbf{A}_m \mathbf{B}_n|}{dx} + \mathbf{E}_4 \frac{d|\mathbf{A}_m \mathbf{B}_{n+q}|}{dx} \right)$$

 $+ E_1 |A|_0 - E_2 |A|_0 p = 0$

But now

(49)
$$|A|_0$$
 (1-x) = $|A| + m |A_m B_n| + m |A_m B_{n+q}|$

(50)
$$p|A| = |B| + n|A_mB_n| + q|A_mB_n + q|$$

and therefore:

$$(49') - |A| \circ = \frac{d|A|}{dx} + m \frac{d|A_mB_n|}{dx} + m \frac{d|A_mB_n+q|}{dx}$$

(50)
$$p|A|_0 = \frac{d|B|}{dx} + n \frac{d|A_mB_n|}{dx} + q \frac{d|A_mB_{n+q}|}{dx}$$

Substitute (49') and (50') in (48):

Simplifying:

$$\frac{d|A_{m}B_{n}|}{dx}\left(-mE_{1} - nE_{2} + E_{3}\right) + \frac{d|A_{m}B_{n}+q|}{dx}\left(-mE_{1} - qE_{2} + E_{4}\right) = 0$$

Now if the reactants have negligible absorption at the wave lengths used then $E_1 = E_2 \cong 0$ and the condition for a maximum in Y which is now a maximum in observed density is:

(53)
$$E_3 \frac{d |A_m B_n|}{dx} + E_4 \frac{d |A_m B_n q|}{dx} = 0$$

In general the maximum value of Y (or density in the last case) will not coincide with the maximum in $|A_mB_n|$ or $|A_mB_n+q|$. The value of x for $\frac{dY}{dx} = 0$ will vary with the extinction coefficients (E) and thus the wave lengths used.

If in equation (53) $E_3 \cong E_4$, the maximum in density corresponds to a maximum in the sum of concentrations of the two complexes then $A_m B_n + q$ is negligible if the stability of $A_m B_n$ is high.

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When volumes of equimolar solutions are mixed, the maximum in density corresponds to the maximum in $[A_m B_n]$ as per (53). If $E_3 >>> E_4$, this latter fact is also true. In dealing with complexes of low stability, however, where E3 and E_4 have no unique relationship, then we may expect a variation with wave length in the x value corresponding to the maximum density. This would be especially true with increasing addition of B.

The method of Job²⁹ allows determination of the complex composition and stability when only one complex is formed. The treatment of Vosburgh and Cooper³⁰ only accounts for complex composition in those cases where unique relations exist among the extinction coefficients of the several complexes viz. equal or widely different. They have also suggested that an asymmetry in the plot of optical density against volume fraction of one of the equimelar solutions is an indication of more than one complex. Also, a variation in the curve maximum with wave length is a valid criterion of the same phenomenon.

4. Other Mathematical Methods of Analysis.

Using spectrephotometric techniques, Hammick and coworkers^{31,32,33} have obtained quantities which are proportional to equilibrium constants when complex stability is low. They have obtained the constant itself in a case of relatively high complex stability.

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The following is based on Hammick's derivation which treats of the case involving only a 1:1 complex.

Consider an equilibrium:

(54) $A + B \rightarrow C$

to be expressed by the mass action law:

(55)

$$K_{1} = \frac{C_{1}}{(A_{0} - C_{1})(B_{0} - C_{1})} = \frac{C_{1}}{L}$$

where A_{\odot} and B_{\odot} are the initial molar concentrations in the solution of A and B molecules and C_{1} is the molar concentration of the 1:1 complex.

Differentiating (55) with respect to A_0 at constant B_0 results in:

(56)

$$O = \frac{(A_{0}-C_{1})(B_{0}-C_{1})\frac{\partial C_{1}}{\partial A_{0}} - C_{1}\left\{(A_{0}-C_{1})(-\frac{\partial C_{1}}{\partial A_{0}}) + (B_{0}-C_{1})(1-\frac{\partial C_{1}}{\partial A_{0}}\right\}}{L^{2}}$$

and thus the numerator is also zero.

Dividing thru by C1 and rearranging:

(57)
$$\frac{\partial C_1}{\partial A_0} \left\{ \frac{(A_0 - C_1)(B_0 - C_1)}{C_1} + (A_0 - C_1) + (B_0 - C_1) \right\} = (B_0 - C_1)$$

Substituting the equilibrium constant for its value (55) and solving for the partial derivative,

(58) $\left(\frac{\mathbf{J} C_{1}}{\mathbf{J} A_{0}} \right)_{B_{0}} = \frac{B_{0} - C_{1}}{\frac{1}{K_{1}} + (A_{0} - C_{1}) + (B_{0} - C_{1})} = \frac{B_{0} - C_{1}}{\frac{1}{K_{1}} + A_{0} + B_{0} - 2C_{1}}$

If C_{\perp} is very small, K_{\perp} is very small and thus $1/K_{\perp}$ is very large with respect to the other terms
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of the denominator and it follows that:

$$\left(\frac{\mathbf{j} \mathbf{c}_{1}}{\mathbf{j} \mathbf{A}_{0}} \right)_{\mathbf{B}_{0},\mathbf{c}_{1} \to \mathbf{0}} \cong \frac{\mathbf{B}_{0}}{\mathbf{K}_{1}} \bullet \mathbf{K}_{1} \mathbf{B}_{0}$$

At constant cell length (1 = 1 cm.), from equation (39)

(60)
$$C_1 = D_1/E_1$$

where E_1 is the extinction coefficient of the complex and D_1 is the observed optical density attributable to the 1:1 complex. Combining (59) and (60) results in:

(61)

$$\begin{pmatrix} 3 & D_{\perp} \\ \hline & J_{A_{\bullet}} \end{pmatrix} \stackrel{\simeq}{=} K_{\perp} E_{\perp} B_{0} \\ B_{0}, C_{\perp} \rightarrow 0$$

This equation means that at constant B_0 and low C_1 , a plot of D_1 against the total unreacted A_0 concontration is a straight line of constant slope $K_1E_1B_0$. Thus K_1E_1 , a value proportional to the equilibrium constant, can be evaluated.

As the amount of C₁ increases, the above approximation becomes less valid and a more accurate approximation of (58) is:

 $\begin{pmatrix} \mathbf{j} \mathbf{c}_{1} \\ \mathbf{j} \mathbf{A}_{0} \end{pmatrix}_{\mathbf{B}_{0}} \cong \frac{\mathbf{B}_{0} - \mathbf{c}_{1}}{\frac{\mathbf{I}}{\mathbf{K}_{1}}}$

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Thus the second partial derivatives becomes:

$$(63) \left[\begin{array}{c} \underbrace{\mathbf{j}} \begin{pmatrix} \mathbf{j} c_{1} \\ \mathbf{j} \mathbf{A}_{\mathbf{0}} \\ \hline \mathbf{j} \mathbf{A}_{\mathbf{0}} \end{array} \right]_{B_{\mathbf{0}}} \cong \frac{1}{\kappa_{1}} \left(- \frac{\mathbf{j} c_{1}}{\mathbf{j} \mathbf{A}_{\mathbf{0}}} \right) = -\kappa_{1} \frac{\mathbf{j} c_{1}}{\mathbf{j} \mathbf{A}_{\mathbf{0}}}$$

or

$$\frac{\frac{\int^{1} C_{1}}{\int A_{0}^{2}}}{\frac{\int^{1} C_{1}}{\int A_{0}}} = \left[\int \frac{\lambda_{n} \left(\frac{\lambda_{0}^{2}}{\int A_{0}} \right)}{\frac{\lambda_{0}}{\int A_{0}}} \right]_{B_{0}} = -K_{1}$$

Again applying (60):
(65)
$$\left[\frac{\partial \ln \left(\frac{\partial D_1}{\partial A_0} \right)}{\partial A_0} \right]_{B_0} = -K_1$$

A plot of the natural log of the instantaneous slope against the corresponding initial concentration of A_0 should give a straight line, the slope of which is the negative value of the equilibrium constant for complex formation. It is significant that there should be a decrease in the slope of the curve of optical density against increasing A_0 .

Hammick presumed that the ratio of $\mathbb{E}_1 \mathbb{K}_1$ values for an homologous series of addition compounds where the \mathbb{K}_1 was too small to determine separately, was independent of the wave length. Such a series qualitatively agreed with one instance where the equilibrium constants were known. However, experimental verification can only be based on constancy of such ratios at varying wave lengths. Maatman⁶ contends that such is not the case.

Maatman⁶ has developed a treatment similar in principle to that involved in application of equation (65) to the quantitative isolation of K_1 for a 1:1 complex.

• Equation (55) can be expanded: (66)

$$K_{1} = \frac{C_{1}}{A_{0}B_{0} - C_{1}A_{0} - C_{1}B_{0} + C_{1}^{2}}$$

Complex concentration (C_1) is assumed to be small and C_1^2 negligible. Ignoring C_1^2 , and rearranging: (67)

$$\frac{A_0B_0}{C_1} - A_0 - B_0 = \frac{1}{K_1}$$

Substituting equation (60) in the above and solving for the extinction coefficient (E_1) :

(68)

$$E_{1} = \frac{D_{1}}{A_{0}} + \frac{D_{1}}{B_{0}} + \frac{1}{K_{1}} + \frac{D_{1}}{A_{0}B_{0}}$$

A similar equation exists for another solution of the same concentration in one reactant, i.e. A_0 , but different in the other, i.e. B_0 ! (69)

$$E_{1} = \frac{D_{1}'}{A_{o}} + \frac{D_{1}'}{B_{o}'} + \frac{1}{K_{1}} + \frac{D_{1}'}{A_{o}B_{o}'}$$

Equating (68) and (69) and solving for $\frac{1}{K_1}$ results in:

(70)
$$\frac{1}{K_1} = \frac{D_1' - D_1}{\frac{D_1}{B_0} - \frac{D_1'}{B_0'}} - A_0$$

In general, A_0 is negligible for small A_0 and K_1 . Maatman⁶ states that the value of the denominator in (70) is small compared to the values of its terms and thus inevitable error in optical measurement leads to very large error in K_1 . Inconsistent results were obtained by Maatman when the data, or averages of the obtained data, were substituted in this equation.

In order to circumvent this large experimental error, Maatman developed the following approximation technique. Equation (68) may be rewritten:

(71)
$$\frac{B_o}{D_1} = \frac{B_o}{A_o E} + \frac{A_o + 1/K}{A_o E}$$

Thus for constant A_0 , $\frac{B_0}{D_1}$ may be plotted against B_0 to approximate a straight line of slope $\frac{1}{A_0E}$. The line thru the points obtainable from experimental data should give the necessary "ideal" values that may be substituted in equation (70) to allow estimation of the magnitude of the equilibrium constant.

Maatman⁶ contends on the basis of his experimental work that the equilibrium constants so calculated are independent of the wave length used.

EXPERIMENTAL

Α. REAGENTS

1. Maleic Anhydride (Eastman)

The anhydride was vacuum distilled at 5mm. A middle fraction of the distillate, b.p. 90°C. was used.

2. Styrene (Dow)

The styrene was vacuum distilled thru a 12 inch Vigreaux column and a fraction 41-43°C at 14-16 mm, $n^{20^{\circ}}$ = 1.5446, $d^{25^{\circ}}$ = 0.907 was used.

All other styrenes were fractionally distilled thru a Fenske column, 10" 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.

3. p-Chlorostyrene (Monomer-Polymer Co.) The fraction 70-72°C at 4.5-5mm, n = 1.5643; d₂₀²⁵⁰ = 1.086 was used.

Literature values:

b.p. 60-62°C at 6.5mm. n^{20°}- 1.5650³⁴ b.p. 38-39°C at 2mm, n^{20°}- 1.5648³⁵ b.p. 200-210°C at 100-120mm b.p. 55-56°C at 3 mm, $n^{20°} = 1.5658$, $d_{40}^{20°} = 1.090^{36}$.

4. p-Methylstyrene (American Cyanamid Co.)

The fraction used:

b.p. 60-70°C at 20.5-22mm, n^{20°}= 1.5425, d^{25°}= 0.889. Literature values: b.p. 59.3-59.5°C at 15.5mm, n^{20°}= 1.5425²¹ b.p. 65-66°C at 18mm, $n^{25°} = 1.5402^{37}$.

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The fraction used:

b.p. 104-108°C at 4-5mm, n^{20°}= 1.6120, d^{25°}= 0.964.

Literature values:

b.p. 85-91°C at 2.5-3mm, $n^{20^{\circ}} = 1.6010^{38}$; $n^{20^{\circ}} = 1.6110$ and $n^{20^{\circ}} = 1.6120^{39}$.

6. p-Methoxystyrene

The p-methoxystyrene was prepared in this laboratory by conversion of 400g. p-anisaldehyde (Eastman) to the corresponding substituted cinnamic acid by means of the Doebner reaction (a modified Perkin reaction with malonic acid, pyridine and ethyl alcohol)⁴¹. The p-methoxycinnamic acid was subsequently decarboxylated over copper powder in quinoline to prepare the p-methoxystyrene according to the method of Walling and Wolfstirn³⁴. The crude yield on decarboxylation from the quinoline was 233.80 grams. On first distillation 182.70 grams were collected at 76-85°C under 6-7mm. This yield is 47.6% based on the aldehyde.

The fraction used:

b.p. 72-73°C at 4-5mm, $n^{20^{\circ}}$ 1.5618-1.5630.

Literature values are:

b.p. 53-53.8°C at 2mm, n^{20°}= 1.5612 and n^{20°}= 1.5620³⁴

 $n^{20^{\circ}}$: 1.5608⁴⁰.

Twenty-two grams of material were chosen from the second distillation for use in the spectrophotometric studies.

7. Benzene (Merck Thiophene free)

The benzene was distilled immediately prior to use. A middle fraction of the distillate was used in the preparation of solutions.

B. PREPARATION OF SOLUTIONS FOR SPECTROPHOTOMETRIC STUDIES

The standard solutions (0.25M and 0.125M) of the substituted styrenes and maleic anhydride for the study of continuous variations were prepared by quantitatively weighing the monomer into a tared beaker, dissolving in the anhydrous benzene and transferring to a glass stoppered volumetric flask. The beaker was subsequently rinsed with successive washings of benzene until the volumetric flask was filled just short of the calibration mark. The flask after shaking was then immersed in a 25°C electronically controlled constant temperature bath for several hours and intermittently agitated to achieve homogenous and thermal equilibrium.

In the preparation of high molar concentrations of the monomers in benzene solution (0.5M and greater), carefully cleaned and dried 50ml. or 100ml. volumetric flasks were tared and the monomers weighed in the flasks.

In the preparation of dilute monomer solutions, (less than 0.1M), requisite amounts of the more concentrated standardized solutions (0.125M and 0.25M) at 25°C were pipetted into volumetric flasks and anhydrous benzene added.

In all the above cases, after the flasks had achieved thermal equilibrium in the 25°C constant

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temperature bath, the few drops of benzene necessary to bring them up to the mark were added and the solutions thoroughly mixed.

In some studies it was necessary to use extremely high concentrations of the substituted styrene (greater than 2.0M) to obtain the desired optical densities. In order to conserve material, the substituted styrene at 25° C was pipetted into a test tube and the number of moles transferred calculated on the basis of the experimentally determined specific gravity at that temperature.

C. PREPARATION OF "COMPLEX" MIXTURES FOR THE STUDY OF CONTINUOUS VARIATIONS

<u>Case 1.</u> Complexes of unsubstituted styrene, p-chlorostyrene and p-methylstyrene with maleic anhydride show no change of optical density with time. With these styrenes, the fractional volumes of the 25°C benzene solution of the styrene and maleic anhydride were added by means of a calibrated burette to a clean, dry test tube fitted with a new, clean cork and then were thoroughly mixed before the readings. The experimental mixtures were poured directly into the absorption cells from the test tubes. The total volume of a mixture was lOml.

<u>Case 2.</u> In the studies on p-dimethylaminostyrene and p-methoxystyrene where there is a change in optical density with time, two methods were used.

(a) In the majority of the p-dimethylaminostyrene studies, the volume of styrene solution wanted was pipetted into the requisite amount of maleic anhydride solution and the timer started when the transfer began. The test tube was corked, shaken several times, and the mixture immediately transferred to the absorption cell for reading of the optical density. The time of each reading was duly recorded.

(b) A modification of (a) to permit quicker observation of the reaction was made by placing the desired amounts of styrene and maleic anhydride solution in separate test tubes, pouring from one to the other at least three times, corking and shaking after each transfer. The timer was started at the moment of the initial transference.

There is no apparent discrepancy in results attributable to these variations in technique.

In all instances of shaking the corked test tube, the cork was loosened and tightened at least twice to prevent loss of material adsorbed on the cork.

The time of mixing and transference usually took 40-70 seconds before the first reading of the optical density could be made.

D. PREPARATION OF "COMPLEX" MIXTURES FOR OTHER STUDIES 1. Studies Under Nitrogen Atmosphere

It was deemed desirable in view of other work in this laboratory to show that complex formation would occur independently of the concentration of absorbed oxygen in the solution. This special study was undertaken with p-methylstyrene.

Nitrogen gas, deoxygenated by passage thru aqueous alkaline pyrogallol and dried by passing thru sulfuric acid, was used to replace the air in all operations. The p-methylstyrene was distilled under a vacuum while a small amount of nitrogen was being introduced into the system, benzene was distilled under a nitrogen atmosphere. Both were stored under a positive nitrogen pressure.

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The maleic anhydride was weighed into a tared volumetric flask previously evacuated and flushed with nitrogen. The flask was then evacuated and flushed several times with nitrogen and the p-methylstyrene and benzene were transferred to the flask by positive nitrogen pressure.

The mixture was transferred by nitrogen pressure to the absorption cells flushed out by nitrogen. The cells were capped immediately and readings were taken as quickly as possible.

2. Effect of Time on Optical Density of "Complex" Mixtures

As has already been mentioned, the optical density of p-dimethylamino and p-methoxystyrene complexes changed rapidly with time and kinetic studies were made on this transformation. Both intermittent and continuous exposure to the light beam show no deviations from a smooth curve when density is plotted against time indicating no photochemical effects. Visual observation of color changes in a portion of the solution not introduced into the light path showed parallel phenomena. Precipitation occurred in the absorption cell simultaneously with that noted in the remaining liquid of the test tube.

Readings on optical density of complexes with

unsubstituted styrene, p-chlorostyrene and p-methylstyrene were continued on the same absorption cell for a period of several hours. This was done with sample mixtures of widely varying concentrations. The cells were subjected to both intermittent and continuous exposure to the light beam. In no instance was any significant change in the optical density manifested that could be attributed to a photochemical effect or a kinetic effect in solution.

Mixtures prepared under nitrogen and in the presence of air were maintained at 25°C for periods of several weeks and readings taken on portions during this time. No significant effects were noted.

3. Effect of Dilution on Optical Density of "Complex" Mixtures.

It was necessary to specifically show the effect of dilution on optical density and this was done with p-chloro and p-methylstyrene mixtures. A series of mixtures was prepared of 5ml. total volume. They were 0.05M with respect to the anhydride and widely variant in molarity of the styrene. Density readings were taken. The contents of the absorption cell were carefully poured back into the test tube which was rinsed with 5ml. of anhydrous benzene. This, too, was poured into the test tube. The tube was shaken and the absorption cell filled and emptied back into the test tube. After a final shaking of the tube, the absorption cell was again filled and the reading taken on the mixture which now had been diluted by half.

E. SPECTROPHOTOMETRIC MEASUREMENTS

All optical density readings below 450 m/ were made in fused silica cells of one centimeter light path with a Model DU Beckman Spectrophotometer. The cells were equipped with caps. Readings above 450 m/ were made in Corex cells with one centimeter light path with a Model B Beckman Spectophotometer. All readings were made at room temperature.

Infra red measurements were made in a Beckman Recording Infra Red Spectrophotometer using a NaCl cell at 25°C.

At the ultra violet and visible wave lengths studied, the absorption of the styrenes did not significantly interfere with the determination of the absorption due to the complex. Beer's law was obeyed by the maleic anhydride solutions (up to 1.00M) and by all the styrenes. The molar extinction coefficients (E) for maleic anhydride in benzene solvents were determined and are listed for the various wave lengths:

TABLE I

MOLAR EXTINCTION COEFFICIENTS FOR MALEIC ANHYDRIDE IN BENZENE

Millimicrons	<u> </u>
375	0.010
370	0.030
365	0.085
360	0.240
355	0.760
3 50	1.64
345	3.63
340	5.94
33 5	9.29
330	15.00
325	24.50
320	33.90

F. INVESTIGATION OF PRECIPITATES FROM SOLUTIONS OF SUBSTITUTED STYRENE AND MALEIC ANHYDRIDE

The precipitate from the benzene solutions of p-dimethylaminostyrene and maleic anhydride was purified by washing with hot benzene in a soxhelet extractor. It was insoluble in all solvents tried: dioxane, petroleum ether, benzene, nitromethane, acetone and methylethylketone. However, the material is readily soluble in NaOH and HCl showing the expected amphoteric properties of compounds with acid anhydride and dimethylamino groups. A liquifying range of 120-130°C was noted.

The precipitate from the benzene solution of p-methoxystyrene and maleic anhydride was washed with cold benzene, hot benzene, cooled and filtered from the liquid. The material is very slightly soluble in hot benzene, readily soluble in acetone and alkali, but not in acids or aliphatic hydrocarbons. The liquifying range was 210-220°C. Attempts at crystallization failed.

G. SUMMARY OF THE EXTENT OF SPECTROPHOTOMETRIC STUDIES

1. Continuous Variations

Benzene solutions of the reactants were prepared, each containing only a single reactant with molarities tabulated in Table II. The given pairs of solutions were then mixed in a varying series of volume fractions. The number of such mixtures made in a series from each pair in the table was 12 to 25. Optical density readings

TABLE II

	SOLUTIONS STUDIED BY CONTINUOUS VARIATIONS:								
"R"	SUBSTITUT	ED STYRI	ene (s) AND	MALEIC	ANHY	DR.	IDE	<u>(M)</u>
R *:	-	н			-01				
Mc	Molarity Wavelengths Molarity Wavelengths					9			
S	М	stuale	ad	S	М	Sti	1016	βα	
0.12	25 0.125	330 to	3 55	0.250	0.250	335	to	3 80	
0.25	50 V.25U	335 to	360	0.500	0.500	34 5	to	3 90	
0.25	50 0.1 25	330 to	360						
0.12	25 0.250	335 to	3 60						
2.00	0.133	340 to	375						
4.27	73 0.100	350 to	375						
8.17	73 0.100	360 to	385						
8.17	73 0.250	365 to	390						

* R is the para substituent of the particular styrene.

R*:	-CH3			-OCH3			
Mola	rity	Wavelengt	:h s	Molari	Lt y W	avelengths	
S	M	stuated		S	M	a rua rea	
0.125	0.500	350 to 4	0 0	0.0500	0.0500	350	
0.250	0.250	340 to 4	00	0.100	0.100	350,375	
0.250	0.500	350 to 4	£00	0.0500	00.100	350 , 375	
0.500	0.125	340 to 4	100	0.100	0.050	350,375,400	
0.500	0.500	360 to 4	£00	0.250	0.050	350,375,400	
2.000	0.250	370 to 4	100	0.050	0.250	350,375,400	

TABLE II (continued)

R:	-N(CH	3) ₂
Molarity		Wave lengths
S	M	stualea
0.250	0.250	500 to 890
0.500	0.250	550
0.250	1.00	550
0.050	1.00	50 0
0.913	0.250	550
0.913	0.050	500

on each mixture were made at five millimicron intervals in the absorption range of the complex. Many series were duplicated to determine reproducibility and establish techniques.

Preliminary volume mixtures of 1:9, 2:8, 3:7, etc. were spectrophotometrically studied to determine the approximate volume ratio giving a maximum optical density. Fractional ratios were then investigated in the vicinity of this maximum.

2. Other Studies

(a) Optical densities were determined with maleic anhydride concentrations ranging up to 1.000M at constant styrene, p-chlorostyrene and p-methylstyrene concentrations: 0.025M and 0.050M.

(b) Additional solutions were studied with p-chlorostyrene concentrations ranging up to 6.270M at 0.050M anhydride concentration. Readings were taken on the same solution after dilution with an equal volume of solvent. This was done similarly with p-methylstyrene concentrations ranging up to 5.3M. All absorbing ultraviolet and visible wave lengths were considered.

(c) Time studies were made for all substituted styrene mixtures with anhydride over wide concentration ranges at all absorbing wave lengths. No density changes were noted for the following benzene solutions of p-methylstyrene and maleic anhydride over a period of three weeks.

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Solutions	Molarity p-methylstyrene	Molarity maleic anhydride	Wave length range studied
l	1.000	0.125	375 - 400
2	0.500	0.125	365 - 400
3	0.250	0.125	355 - 400
4	1.493	0.250	385 - 400

(d) Measurements were taken of change in extinction with time for all mixtures studied under the continuous variation of p-dimethylaminostyrene and p-methoxy-styrene with maleic anhydride. In addition solutions with the following concentrations of reactants were studied between 350 and 390 m μ .

Solution	Molarity p-dimethylamino- styrene	Molarity maleic anhydride
l	0.0250	0.0250
2	0.0250	0.0125
3	0.0125	0.0250
4	0.0125	0.0125

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(e) Infra red scannings were made of the following solutions:

Solution	Molarity Styrene	Molarity anhydride
1	0.500M	0.000
2	0.000	0.500
3	0.500	0.500
4	pure styrene	0.000
5	pure styrene	0.500

(f) The following solutions were prepared under nitrogen and no density charges were noted over a period of three weeks.

Solution	Molarity p-methylstyrene	Molarity anhydride	
A	0.453	0.125	
В	0.751	0.125	
С	1.500	0.125	

Readings

mµL	Density A Complex	Density B Complex	Density C Complex
4 00	0.058	0.116	0.198
390	0.169	0.302	0.569
380	0.417	0.717	1.375
375	0.627	1.063	2.033
370	0.915	1.531	
365	1.266	2.092	
360	1.716		

INTERPRETATION OF RESULTS

INTERPRETATION OF RESULTS

A. THE METHOD OF CONTINUOUS VARIATIONS

As has been explained in a prior section, this method involves the determination of optical densities of a continuous series of styrene and maleic anhydride mixtures. The sum of the values of the optical density due to the unreacted maleic anhydride and the styrene are subtracted from the observed density values. This increase in the value of the optical density is due to the complex's absorption in the benzene solvent and is plotted as (D) against the fractional volume of the maleic anhydride solution in the mixture (x). The (x)value of the maximum, when equimolar solutions are continuously varied indicates the ratio of the reactants in the complex. For non-equimolar solutions where the equilibrium constant is significant and calculable, the (x) maximum should be displaced from this prior value of (x). Interpretation of equation (21) shows that for a more highly concentrated solution of the styrene, the maximum should be displaced toward the greater volume fraction of the maleic anhydride solution (i.e. greater (\mathbf{x})) and conversely.

Figures 1 thru 6 are representative of continuous variations of the various styrene mixtures with maleic anhydride at all wave lengths where the complexes absorb.



CONTINUOUS VARIATIONS

MALEIC ANHYDRIDE AND P-METHYLSTYRENE

375m U



CONTINUOUS VARIATIONS

MALEIC ANHYDRIDE AND P-CHLOROSTYRENE

	375 m 🕰	
Curve	M Anhydride	M Styrene
A	0.250	0.250
В	0.500	0.500



CONTINUOUS VARIATIONS

MALEIC ANHYDRIDE AND P-METHOXYSTYRENE

(375 mµ)





FIGURE 5



There were no discernible deviations in the types of curves obtained by the method of continuous variations. The choice of wave lengths to represent the method in the figures was based solely on the advantageous spanning of the range of optical densities at the concentrations studied.

It has been previously mentioned and will be discussed further in a later section that the light absorption of p-methoxystyrene and p-dimethylaminostyrene solutions with maleic anhydride change with time. To apply this method the extinction values were extrapolated to zero time and these values taken as being due to the primary complex formation. This necessarily introduced a large element of error, specifically in the case of the p-methoxystyrene which gave the greater rate of change. Also, relatively greater anhydride concentration of p-methoxystyrene gave a large initial rate of increase in optical density. Thus, the more anhydride, the greater was the error and Figure 4 is not too conclusive.

The equimolar curves (1-A, 2-A, 2-C, 3-A, 3-B, 5-A and 5-C) for the other styrene complexes give a maximum at x = 0.5 proving conclusively the presence of a 1:1 complex. Time studies on the complexes of unsubstituted styrene, p-chlorostyrene and p-methyl-styrene show no change of optical density and thus in all cases studied (including the p-dimethylamino-styrene) the complexes are instantaneously formed.

The continuous variation of non-equimolar solutions show no appreciable shift in the maximum

-43-

(x = 0.5) for the unsubstituted styrene, p-chlorostyrene and p-methylstyrene cases indicating extremely low stability of the complexes.

Curves (2-B, 2-D) for p-methylstyrene are still symmetrical and give no indication of a shift.

According to Vosburgh and Cooper³⁰ curve symmetry is a strong argument for a unique complex. Curves (1-C, 1-D) with higher styrene concentration for the unsubstituted styrene cases are unsymmetrical. The indicated shift in the maximum is not toward increasing (x) values as should be expected for a unique 1:1 complex but toward decreasing (x) values. Application of equation (21) would result in a negative equilibrium constant! This is a positive indication of further interaction of the 1:1 complex with styrene.

Only the p-dimethylaminostyrene complex appears amenable to calculation of the equilibrium constant in this manner. The symmetrical equimolar curves of Figure 5 indicate the existence of a unique 1:1 complex. The direction of the shifts in the maxima of the nonequimolar curves in Figure 6 are normal. Although the shifts are small and the error therefore large, yet the direction of the shifts are opposed for one or the other reactant in excess (pairs 6-A and 6-B). We may arrive at the magnitude of the complex's stability in this case using equation (21).

Since m = 1, n = 1, equation (21) becomes:

$$K_{D} = \frac{[A_{D} [(1+p)x-1]^{2}}{(p-1)(1-2x)}$$

and using the data where $B_0 = p A_0$,						
Styrene	MA	p	x	К _D	кı	
Ao	B _o					
0.250	1.000	4.00	0.467	2.25	0.45	
0 .913	0.250	0.274	0.533	1.98	0.51	
0.050	1.000	20.0	0.450	1.89	0.53	
0.913	0.050	0.0548	0.533	2.8	0.36	

 K_D is the value of a disocciation constant and thus the average $K_1 = 1/K_D = 0.46$ represents the equilibrium constant.

This calculation of the equilibrium constant is only valid when a large amount of complex is formed and only the relative magnitude can be claimed in this instance. The increased error in extrapolation to zero time with higher concentration differences between the dimethylaminostyrene and anhydride did not warrant such studies.

B. EVALUATION OF THE FURTHER INTERACTION OF A 1:1 COMPLEX WITH THE REACTANTS

1. Development of a Quantitative Interaction Theory I

The method of "continuous variations" has shown that only in one instance (p-dimethylaminostyrene) is the complex stability sufficient to warrant estimation of the magnitude of the equilibrium constant by this method. Certain anomalies in the symmetry of the curves and the shift in the maxima indicate an interaction of the proven 1:1 complex with a reactant (viz. with styrene in Fig. 1). It may be proposed, on the basis of these observations, that another complex is formed which also absorbs at the wave lengths studied.

Postulating this interaction in terms of a further equilibrium in addition to (54) i.e.

(72) $C_1 + n \land \rightarrow C_2$

where C₂ = A n+1 B, then

$$\binom{(73)}{K_2} = \frac{C_2}{C_1(A_0 - C_1)^n}$$

Using the value of C_1 in (55) and rearranging: (74)

$$K_{1}K_{2} = \frac{C_{2}}{(A_{0} - C_{1})^{n+1}(B_{0} - C_{1})} = \frac{C_{2}}{L_{1}}$$

Differentiating (74) with respect to A_0 at constant B_0 results in (75) $O = (A_0 - C_1)^{n+1} (B_0 - C_1) \frac{C_2}{J_{A_0}} - C_2 \left\{ (A_0 - C_1)^{n+1} \left(-\frac{J_0 C_1}{J_{A_0}} \right) \right\}$

$$+ (n+1) (B_0 - C_1) (A_0 - C_1)^n \left(1 - \frac{\partial C_1}{\partial A_0}\right) \right\}$$

Dividing thru by C_2 and rearranging: (76)

$$\frac{\partial C_2}{\partial A_0} \left[\frac{(A_0 - C_1)^{n+1} (B_0 - C_1)}{C_2} \right] + \frac{\partial C_1}{\partial A_0} \left[(A_0 - C_1)^{n+1} \right]$$

+
$$(n+1)(B_0-C_1)(A_0-C_1)^n$$
 = $(n+1)(B_0-C_1)(A_0-C_1)^n$

Substituting the equilibrium constants for their values in (55) and (74) and multiplying thru by

 $\frac{\frac{K_{1}}{A_{0}-C_{1}}}{\binom{77}{\frac{3}{A_{0}}C_{2}}{(A_{0}-C_{1})^{n-1}}} + \frac{3C_{1}}{3C_{0}} \left[K_{1}(A_{0}-C_{1})^{2}+C_{1} \right] = (n+1)C_{1}$

For both K_1 and K_2 small, the second term is negligible since $\left(\frac{\int C_1}{\int A_0}\right)_{B_0} \cong K_1(B_0-C_1)$ in equation (62) and

$$\binom{(78)}{\binom{3}{2}C_2} = K_2(n+1) C_1(A_0 - C_1)^{n-1}$$

Now the total optical density observed (D_t) is the sum of the densities attributable to all the complexes present and thus (79)

$$\frac{\partial D_{t}}{\partial A_{0}} = \frac{\partial D_{1}}{\partial A_{0}} + \frac{\partial D_{2}}{\partial A_{0}} + \frac{\partial D_{3}}{\partial A_{0}} + \cdots$$

where D_2 is the optical density due to the further interaction of the 1:1 complex with (n) molecules of (A). As in equation (60),

(80)

$$C_2 = \frac{D_2}{E_2}$$

and (78) becomes

(81)

$$\left(\begin{array}{c} \mathbf{D}_{2} \\ \mathbf{J}_{A_{OB_{O}}} \end{array}\right) = \mathbf{E}_{2}\mathbf{K}_{2}(\mathbf{n+1})\mathbf{C}_{1} (\mathbf{A}_{O}-\mathbf{C}_{1})^{\mathbf{n-1}}$$

Substituting (61) and (81) into (79) for small K_1 and C_1 , assuming only one additional complex, (82)

$$\left(\frac{\mathbf{J} \mathbf{D}_{t}}{\mathbf{J} \mathbf{A}_{0} \mathbf{B}_{0}} = \mathbf{E}_{1} \mathbf{K}_{1} \mathbf{B}_{0} + \mathbf{E}_{2} \mathbf{K}_{2} (\mathbf{n}+1) \mathbf{C}_{1} \mathbf{A}_{0}^{\mathbf{n}-1}$$

On the same conditions, (55) allows (83)

$$C_1 = K_1 A_0 B_0$$
 which modifies (82) to

(84)

$$\left(\frac{\mathbf{J} \mathbf{D}_{t}}{\mathbf{J} \mathbf{A}_{0} \mathbf{B}_{0}} = \mathbf{E}_{1} \mathbf{K}_{1} \mathbf{B}_{0} + \mathbf{E}_{2} \mathbf{K}_{1} \mathbf{K}_{2} (\mathbf{n+1}) \mathbf{A}_{0}^{\mathbf{n}} \mathbf{B}_{0}$$
Taking the second partial derivative,

(85)

$$\left(\frac{\partial^{2} D_{t}}{\partial A_{0}^{2}}\right)_{B_{0}} = E_{2} K_{1} K_{2} (n+1) n A_{0}^{n-1} B_{0}$$

The (n+1) derivative is

(86)

$$\left(\frac{j^{n+1}D_{t}}{j_{A_{0}}^{n+1}}\right)_{B_{0}} = E_{2}K_{1}K_{2}(n+1)!B_{0}$$

If a third complex were present and had significant absorption the (n+2) derivative would have eliminated the contributions of the first and second complexes end the subsequent remarks would then be applicable to the third since the above treatment can be expanded for its consideration.

The postulates for the utilization of equations (82) thru (86) are very small K_1 , low C_1 and significant values of E_2K_2 .

For low B_0 and A_0 , C_1 concentration is negligible and equation (22) reduces to the Hammick simplified case (61) for a unique 1:1 complex.

(87)

$$\begin{pmatrix} \underbrace{\mathbf{J}}_{\mathbf{L}}^{\mathbf{D}} \\ \underbrace{\mathbf{J}}_{\mathbf{A}_{\mathbf{0}}}^{\mathbf{D}} \\ B_{\mathbf{0}}, C_{\mathbf{1}} \rightarrow 0 \end{pmatrix} = \begin{pmatrix} \underbrace{\mathbf{J}}_{\mathbf{1}}^{\mathbf{D}} \\ \underbrace{\mathbf{J}}_{\mathbf{A}_{\mathbf{0}}}^{\mathbf{D}} \\ B_{\mathbf{0}}, C_{\mathbf{1}} \rightarrow 0 \end{pmatrix} \cong \mathbf{E}_{\mathbf{1}} \mathbf{K}_{\mathbf{1}} \mathbf{B}_{\mathbf{0}}$$

This signifies that the initial slope of the plot of the observed optical density at a constant concentration (B_0) of one reactant against the varied concentrations of the second (A_0) can be used to evaluate the E_1K_1 product for the 1:1 complex.

If further interaction of the 1:1 complex with more (A) occurs, the curve deviates from linearity with an increasing slope as shown by equation (84). If the second complex is A_2B (i.e. n = 1), equation (85) reduces to

(88)

$$\left(\underbrace{\mathbf{\hat{J}}_{\mathbf{D}_{t}}}_{\mathbf{A}_{0}}\right)_{\mathbf{B}_{0}} = 2 \mathbf{E}_{2}\mathbf{K}_{1}\mathbf{K}_{2}\mathbf{B}_{0}$$

This means that a graphing of the slope in the curve obtained above against the A_0 concentration should approximate a straight line. The slope of this new line should be the value of $2 E_2 K_1 K_2 B_0$ since B_0 is constant.

If the new line is still a parabola of increasing slope, the process can be repeated and from the n+1 curves drawn to obtain a straight line the formula $A_{n+1}B$ of the second absorbing complex can be determined.

The value of (n) can be obtained more simply by plotting the log of the varying slopes (from the graph representing equation (84) against the log of the corresponding A_0 concentration. As per (89)

$$\log\left(\frac{\mathbf{b} \mathbf{b}}{\mathbf{b}_{A_0}}\right) = \operatorname{nlog} \mathbf{A}_0 + \log \mathbf{E}_2 \mathbf{K}_1 \mathbf{K}_2 (\mathbf{n+1}) \mathbf{B}_0$$

The slope of this line is the value of (n).

Greater magnitude of K_1 with respect to K_2 invalidates this treatment of the contribution of further complex interactions.

Assuming significant C_1 with increasing concentrations of the reactants the more accurate equation (62) should be used instead of (61). Then (78) is still valid but (82) becomes: (90)

$$\left(\frac{\partial D_{t}}{\partial A_{o_{B_{o}}}}\right) = E_{1}K_{1}(B_{o}-C_{1}) + E_{2}K_{2}(n+1)C_{1}(A_{o}-C_{1})^{n-1}$$

+ $E_1K_1(B_0-C_1) + E_2K_1K_2(n+1)(A_0-C_1)^n(B_0-C_1)$

and for A_2B where n = 1, (91)

$$\begin{pmatrix} \mathbf{J}^{\mathrm{D}_{\mathrm{t}}} \\ \mathbf{J}_{\mathrm{A}_{\mathrm{o}_{\mathrm{B}_{\mathrm{o}}}}} \end{pmatrix} = \mathbb{E}_{1} \mathbb{E}_{1} \mathbb{E}_{0} - \mathbb{C}_{1} + 2 \mathbb{E}_{2} \mathbb{E}_{1} \mathbb{E}_{1} \mathbb{E}_{0} - \mathbb{C}_{1} \times \mathbb{E}_{0} \mathbb{E}_{1} \mathbb{E}_{0} - \mathbb{C}_{1} \times \mathbb{E}_{0} \mathbb{E}_{0} = \mathbb{E}_{1} \mathbb{E}_{0} \mathbb{E}_{0} = \mathbb{E}_{0} \mathbb{E}_{0} \mathbb{E}_{0} = \mathbb{E}_{0} \mathbb{E}_{0} \mathbb{E}_{0} = \mathbb{E}_{0} \mathbb{E}_{0} \mathbb{E}_{0} \mathbb{E}_{0} = \mathbb{E}_{0} = \mathbb{E}_{0} = \mathbb{E}_{0} \mathbb{E}_{0} = \mathbb$$

The significant value of C_1 lessens the slope of the plot of observed density against A_0 in a manner similar to Hammick's 1:1 complex (equation (62)). The tendency for the second complex's contribution to increase the slope is also lessened. No conclusive statement as to additional interactions can be made about such systems where the above plot is linear as it may be just a fortuitous balancing of effects.

Fow low C_1 , small K_1 and significant values of E_2K_2 ', this development can be used to recognize dimers in equilibrium with the complex. Defining K_2 ' by

(92)
$$K_2' = \frac{C_2'}{C_1(A_0-C_1)(B_0-C_1)} = \frac{C_2'}{K_1(A_0-C_1)^2(B_0-C_1)^2}$$

Then, corresponding to (88), (93) $\left(\frac{\partial^2 D_t}{\partial A_0^2}\right)_{B_0} = 2 E_2 K_1 K_2 B_0^2$

A similar equation is valid when B_0 and A_0 are interchanged. For a series of constant B_0 's, the representative slopes would have to be divided by B_0^2 to give equal values rather than by B_0 as in equation (88).





Figure 8



Figure 9

DENSITY VS. P-CHLOROSTYRENE

CONSTANT ANHYDRIDE (375m A)





Figure 11



DENSITY VS. P-METHYLSTVRENE

CONSTANT ANHYDRIDE

(375mA)



Figure 13



Figure 14

2. Application of the Interaction Theory I to the Studied Complexes

Observed optical densities (D_t) were plotted against the molarity of the complexing styrene (S_0) at constant maleic anhydride concentration (M_{n}) for each wave length studied. Typical examples for styrene, p-chlorostyrene and p-methylstyrene are respectively shown in Figures 7, 10, and 13. Increasing slopes in the first two cases indicate further interaction with the hydrocarbon as per equation (84). Observed optical densities (D_t) plotted against the molarity of the maleic anhydride (M_0) for the converse case (i.e. styrene molarity constant) shows no observable deviations from linearity in Figures 9, 12 and 14. No further interaction of the 1:1 complex with the anhydride can be deduced from this analysis. Because of solubility difficulties in handling anhydride concentrations greater than 1.0M in benzene, this was the maximum concentration used.

The value of (n) for the postulated additional complex with styrene is unity by application of equation (89) and the only other significant complex is of the formula MS₂.

With graphs similar to the sample Figures 7, 10 and 13 for constant anhydride concentration the values of the initial slopes and E_1K_1 values can be determined as per equation (87) for all wave lengths. Division of each initial slope $(E_1K_1M_0)$ by its respective constant maleic anhydride molarity (M_0) should give a constant E_1K_1 if the theory is valid. This is shown to be true in columns (a), (d) and (g) of Table III for sample cases. These E_1K_1 values are also shown to be the same as those determined from Figures 9, 12 and 14 for constant styrene (S₀) molarities (columns (b), (e) and (h)).

The theory is applied further in the two cases of observed interaction with the styrene hydrocarbon, Figures 8 and 11, styrene and p-chlorostyrene. The straight line resulting from the plot of $\frac{1}{2}D_t$ vs. molarity of the styrene (S₀) shows that $\frac{1}{2}S_0$ n = 1 and reduces equation (85) to (88). Division of the slope ($2E_2K_1K_2M_0$) by twice the respective constant anhydride molarity ($2M_0$) gives the constant $E_2K_1K_2$ predicted by the derivation as shown in columns (c) and (f).

More accurate $E_{1}K_{1}M_{0}$ values may be obtained from the intercept of this line.

 E_1K_1 values are similarly determined from the zero time extrapolated density values for the p-methoxy and p-dimethylaminostyrene complexes.

TABLE III

SAMPLES OF REPRODUCIBILITY OF EVALUATED CONSTANTS

BY INTERACTION THEORY I

Molarity		Styren	8	p-Ch	lorost	yrene	p-M	ethyl-
Constant Reactant	(a) E _l K _l	(ъ) Е ₁ К1	(c) E ₂ K1K2	(d) ^E 1 ^K 1	(e) E l ^K l	(f) E ₂ K ₁ K	sty: (g) 2 ^E 1 ^K 1	rene (h) E ₁ K1
0.015	2.03 (8A)		0.09 (8A)					
0.025	(8B)	5.72 (9A)	(8B)	2.39 (10A)	2.63 (12A)	0.23 (11A)	11.3 (13A)	11.8 (14A)
U.03 0 0.040	1.87 (8C) 1.81	١	0.10 (8C) 0.11					
0.050	(7A,8D 1.74 (8E)	5.75 (9B)	0.12 (8E)	2.40 (10B)	2.44 (12B)	0.29 (11B)	11.1 (13B)	11.8 (14B)
U.070	(7B,8F 1,79)	(8F) 0.12					
0.075	(89)		(60)				11.9	11.2
0.080	1.80		0.14					
0,100	(on)		(811)				10.9	11.4
0.125							11.2	10.7

Average 1.85 5.73 0.12 2.40 2.53 0.26 11.3 11.3

(a) and (c) at 370 m Mat constant anhydride molarity

(b) at 360 m/4 at constant styrene molarity

(d), (f) and (g) at 375 mµ at constant anhydride molarity

(e) and (h) at 375 mµat constant syrene molarity

N.B. The parenthesis after the datum contains a Figure number and curve letter to which the constant can be referred.

3. Another Interaction Theory (II) and its application

The graphical estimation of incremental slopes is a tedious process and a more simplified but less elegant treatment can be developed.

Postulating only a 1:1 complex (54) the expression of the mass action law (66) may be rearranged to: (94)

$$K_1 \frac{A_0 B_0}{C_1} - (A_0 + B_0) K_1 + C_1 K_1 = 1$$

Substituting (60) for C₁ and rearranging

(95)

$$E_1K_1 \frac{A_0B_0}{D_1} = 1 + K_1(A_0 + B_0) - \frac{K_1}{E_1} D_1$$

When K_1 is very small and C_1 is small (95) can be restated:

$$\frac{(96)}{D_1} = \frac{1}{\mathbf{E}_1 \mathbf{K}_1}$$

which means that for low A_0 and B_0 concentrations, the product of the initial concentrations of the reactants divided by optical density attributable to the complex is a constant.

As the concentrations of one or both of the reactants increases, only the final term of (95) remains negligible and the valid equation is (97)

$$\frac{A_{0}B_{0}}{D_{1}} = \frac{1}{E_{1}K_{1}} + \frac{1}{E}(A_{0} + B_{0})$$

where the plot of $\frac{A_0B_0}{D}$ vs. $A_0 B_0$ will give a slope

of $1/E_1$ and an intercept of $1/E_1K_1$. The large values of intercept and the low value of the slope probably will not warrant the determination of these constants by this method. However, the resulting curve has a decidedly negative slope. Then it can be surmised that absorption is occurring beyond that attributable to the l:l complex. Rearranging (95) gives:

(98)

$$\frac{D_1}{E_1 K_1 A_0 B_0} = \frac{1}{1 + K_1 (A_0 + B_0) - \frac{D_1 K_1}{E_1}}$$

If the total density (D_t) is the sum of the contributions from several complexes.

(99)

 $D_t = D_1 + D_2 + ...$

Considering only two, substituting the value of D_1 into (98) and rearranging

$$\frac{D_{t}}{E_{1}K_{1}A_{0}B_{0}} = \frac{1}{1+K_{1}(A_{0}+B_{0})} - \frac{D_{1}K_{1}}{E_{1}} + \frac{D_{2}}{E_{1}K_{1}A_{0}B_{0}}$$

As in the interaction theory I, D_2 is the optical density of the second complex C_2 and from equation (74) and (80) when n = 1, K_1 and C_1 are small.

(101)

[′] D₂ **°** E₂K₁K₂A₀²B₀

Substituting (101) in (100), simplifying and putting over a common denominator (102)







Figure 16

(102)

$$\frac{D_{t}}{E_{1}K_{1}A_{0}B_{0}} = \frac{1 + \left[1 + K_{1}(A_{0} + B_{0}) - \frac{D_{1}K_{1}}{E_{1}}\right] \frac{E_{2}}{E_{1}} K_{2}A_{0}}{1 + K_{1}(A_{0} + B_{0}) - \frac{D_{1}K_{1}}{E_{1}}}$$

If $\frac{E_2}{E_1}K_2$ or A_0 is very small relative to K_1 , (102) reverts to (98). If K_1 is also small (97) is valid. If attempts to use (97) resulted in a line of negative slope then the converse is true and K_1 is very small relative to $\frac{E_2}{E_1}K_2$. The final two terms of the denominator are negligible and at low B_0 (102) reduces to:

 $\frac{D_{t}}{E_{1}K_{1}A_{0}B_{0}} = \frac{1 + \frac{E_{2}}{E_{1}} K_{2}A_{0}}{E_{1}}$

or

(104)

$$\frac{D_{t}}{E_{1}K_{1}} = E_{1}K_{1} + E_{2}K_{1}K_{2}A_{0}$$

A plot of $\frac{D_t}{A_0B_0}$ vs. A_0 will evaluate the same constants as interaction theory I, a slope of $E_2K_1K_2$ and an intercept of E_1K_1 . Figures 15 and 16 represent such plots for styrene and p-chlorostyrene complexes and give the predicted straight line when $\frac{D_t}{S_0M_0}$ is plotted against the styrene concentration (S_0) at low maleic anhydride concentration (M_0) . No unique relationship was apparent with the other substituted styrene complexes.

<u>4. AN INTERMEDIATE CASE:</u> <u>Complexes of p-Methylstyrene and Maleic Anhydride.</u> <u>Interaction Theory III</u>

It has been shown in equations (91) and (102) that if K_1 and C_1 are too large, the Interaction Theories (I and II) cannot be satisfactorily applied. If a second complex strongly absorbs and/or K_1 is not large enough, the method of continuous variations cannot be applied to the determination of the equilibrium constant K_1 . None of these methods of analysis satisfactorily applied to the p-methylstyrene complex at all wave lengths. This indicates one of the following:

(a) Only a 1:1 complex is formed of low K_1 so that the maximum in optical density is not significantly shifted with respect to (\mathbf{X}) in non-equimolar continuous variations, even with large differences in the molarities of the two solutions (Curve 2D).

(b) Additional complexes are also formed but K_1 and C_1 are significant with respect to $\frac{E_2}{E_1} K_2$ and the previous Interaction Theories $\frac{E_1}{E_1}$ developed are not applicable.

An attempt to apply Interaction Theory I at higher wave lengths resulted in approximate $E_2 K_1 K_2$ values of 0.05 at 390, 395 and 400 mga. As can be seen from Table III, this is barely within the range of reproducibility. It cannot be considered as conclusive evidence for further interaction, especially







since the phenomenon can only be observed in one region of the spectrum due to complex. An expansion of Maatman's ⁶ approximation technique has been applied in an attempted clarification.

Graphs of equation (71) were made and typical examples are shown in Figures 17 and 18. The equation states that a plot of $\frac{B_0}{D_1}$ vs. B_0 at constant A_0 should give a $\frac{B_0}{D_1}$ straight line. In Figure 17, $B_0 = M_0$ (molarity of anhydride) and $A_0 = S_0$ (molarity of the styrene) in a solution of density D_t at 350 m/M. The "ideal" curve drawn thru these points serves to minimize experimental error in optical measurements. "Ideal" data chosen from the extremes of the line is substituted into equation (70) to calculate K_1 . Maatman states that for a 1:1 complex the K_1 values thus arrived at should not vary with the wave length.

"K₁" values determined in this manner at constant styrene concentrations are tabulated in Table IV for the various wave lengths. The plotted data approximates the predicted straight line only at the lower wave lengths studied (350 - 360 m/ μ). At 360-370 m/ μ the curves tend to bend over with increasing anhydride concentration (M₀). No correlation is perceived at any higher wave length.

According to Maatman's hypothesis, similar plots of S_0/D_t vs. S_0 at constant M_0 should give the same curves as before for a 1:1 complex. Only at these lowest wave lengths studied did the data hug the

"ideal" line so that correlation could be ascertained. The bending over, i.e. decreasing slope of the plots was also manifested in Figure 18 and in instances where lines could be objectively drawn, their slopes were much lower than those drawn at constant styrene concentration. In general, the magnitude of the deviations from the "ideal" line enormously increases with increasing wave length.

This surprising discrepancy between the curves at constant p-methylstyrene and constant anhydride is shown by the columns for the apparent "K1" values calculated from (M_0) at different wave lengths. The starred values were calculated from "ideal" lines that showed very poor correlation with the actual data.

It will be noted, however, that these apparent "K1" values show a decided increase with decreasing wave length. This can be explained by the following extension of Maatman's thesis.

The optical density D_1 in equation (71) is (D_t) , the sum of several contributions (99). Considering two for purposes of discussion and using the same postulates that lead to equation (102), we have on inversion of the equation and dividing thru by Borlk1

$$\frac{A_{o}}{D_{t}} = \frac{\frac{A_{o}}{E_{1}B_{o}} + \frac{B_{o} 1/K_{1}}{E_{1}B_{o}}}{1 + \left[1 + K_{1}(A_{o} + B_{o})\right] \frac{E_{2}}{E_{1}} K_{2}A_{o}}$$

Δ

which is (71) when $\frac{E_2}{E_1} K_2 = 0$

This equation shows that if AB interacts further with A that the plot of A_0/D_t vs. A_0 will not give a straight line but a curve of decreasing slope with increasing A. This leads to the interpretation that both maleic anhydride and p-methylstyrene interact with the 1:1 complex, the latter more appreciably than the former and accounts for the observed phenomena discussed above. As $\frac{E_2}{E_1}$ K₂ increases, the deviation from the linearity expected by equation (71) becomes more marked. An "ideal" straight line would average a smaller slope, and the calculated apparent " K_1 " values would decrease. On this basis, there is strong indication that at the higher wave lengths the absorption (E_2) of the second complex has increased relative to that (E_1) of the first. This also explains the fact that application of Interaction Theory I may be possible at higher wave lengths since the premises of its derivation are more aptly fulfilled.

The extent of this interaction can be surmised if an approximate value of the true K_1 is known.

Again inverting (102) and dividing by $\frac{K_1}{D_t A_0 B_0}$ where $C_1 - \frac{D_1}{E_1}$ and K_1 is not too large,

(106)

$$E_{1} = \frac{1}{K_{1}} \frac{D_{t}}{A_{0}} + \frac{D_{t}}{B_{0}} + \frac{D_{t}}{A_{0}}$$
For a second

$$1 + \frac{E_{2}}{K_{1}} K_{2} A_{0}$$
set of values
at constant B_{0} ,
an equation

(107) can be written with D_t and A_0 .

Equating (106) and (107) and rearranging (108)

$$\frac{1}{K_1} = \left[D_t' - D_t + \frac{D_t' B_o}{A_o'} - \frac{D_t B_o}{A_o} \right]$$

+
$$\frac{\mathbf{E}_2}{\mathbf{E}_1} \mathbf{K}_2 \left[\mathbf{A}_0 \mathbf{D}_t' - \mathbf{A}_0' \mathbf{D}_t + \frac{\mathbf{A}_0 \mathbf{B}_0 \mathbf{D}_t'}{\mathbf{A}_0'} - \frac{\mathbf{A}_0' \mathbf{B}_0 \mathbf{D}_t}{\mathbf{A}_0} \right]$$

divided by

$$\left[\frac{D_{t}}{A_{o}} - \frac{D_{t}'}{A_{o}'}\right] + \frac{E_{2}}{E_{1}} \kappa_{2} \left[\frac{A_{o}'D_{t}}{A_{o}} - \frac{A_{o}D_{t}'}{A_{o}'}\right]$$

If $\frac{E_2}{E_1} K_2 \rightarrow 0$ then (108) reduces to (70). If a true E_1 value of K_1 is known, then from the values of D_t , D_t ', A_0 and A_0 ' determined from the "ideal" curve which is a straight line approximation of (105), an approximation of $\frac{E_2}{E_1} K_2$ can be made as: (109)

$$\frac{\mathbf{E}_{2}}{\mathbf{E}_{1}} = \frac{\begin{bmatrix} \mathbf{D}_{t}' - \mathbf{D}_{t} + \frac{\mathbf{D}_{t}' \mathbf{B}_{0}}{\mathbf{A}_{0}'} - \frac{\mathbf{D}_{t} \mathbf{B}_{0}}{\mathbf{A}_{0}} - \frac{1}{\mathbf{K}_{1}} \begin{bmatrix} \frac{\mathbf{D}_{t}}{\mathbf{A}_{0}} - \frac{\mathbf{D}_{t}'}{\mathbf{A}_{0}'} \end{bmatrix}}{\frac{1}{\mathbf{K}_{1}} \left(\frac{\mathbf{A}_{0}' \mathbf{D}_{t}}{\mathbf{A}_{0}} - \frac{\mathbf{A}_{0} \mathbf{D}_{t}'}{\mathbf{A}_{0}'} \right) - \left(\mathbf{A}_{0} \mathbf{D}_{t}' - \mathbf{A}_{0} \mathbf{D}_{t} + \frac{\mathbf{A}_{0} \mathbf{B}_{0} \mathbf{D}_{t}'}{\mathbf{A}_{0}'} - \frac{\mathbf{A}_{0}' \mathbf{B}_{0} \mathbf{D}_{t}}{\mathbf{A}_{0}} \right)}$$

and all values are known.

If B_0 is small and since $A_0D_t \cong A_0D_t$ then (109) becomes

(110)

$$\frac{E_2}{E_1} K_2 = \frac{(K_1 - "K_1")(D_t' - D_t)}{\frac{A_0'D_t}{A_0} - \frac{A_0D_t'}{A_0'}}$$

TABLE IV A

REPRODUCIBILITY OF EVALUATED CONSTANTS FOR

	<u>P-M</u>	ETHYLSTYR	ENE COM	PLEXES BY	r	
		INTERACI	ION THE	ORY III		
Molarity	At	Constant	p-Meth	ylstyrene	Ð	
Constant		375	mu	370m	<u>(</u>	
		(A)	(B)	(A)	(B)	
0. 025		**		0.08#	0.30	
0.05		**		0.07	0.30	
						_
	(A) 36	60m/(B)	(A) ³	55m/((B)	(A) ³⁵	;Om U
9. 025	0,18	0,19	0,20	0.14	0.36	
0.05	0.16	0.21	0.29	0.09	0.40	

* "ideal" lines showed very poor correlation with available data.

** available data apparently random.

(A) Calculations for " K_1 " based on equation (70)

(B) Calculations for $\frac{E_2}{E_1} K_2$ based on equation (110)

assuming $K_1 = 0.40$

TABLE IV B

REPRODUCIBILITY OF EVALUATED CONSTANTS FOR

P-METHYLSTYRENE COMPLEXES BY

INTERACTION THEORY III

Molarity	At	Consta	nt Maleic	Anhydri	de
Constant Reactant	(A)	375m/	(B)	(A) <u>37</u>	Om µ (B)
0.025	**			0.013 ⁸	0.37
0.05	0.03		0.36	0.022*	0.37
0.075	**				
0.125	0.08#	•	0.31	0.142 ^b	0.24
_					
-	-				
	(A) 360	mμ (B)	(A) <u>35</u>	5mµ (B)	(A)
0.025	0.023*	0.18	0.036 ^a	0.34	0.042*
0.05	0.13*	0.31	0.21*	0.16	0.48 ^b
0.075	0.21	0.34	0.61 ^b	**	**
0.125	0.33	0.07			0.44 ^b

* "ideal" lines showed very poor correlation with available data.

** available data apparently random.

0.125 0.33 0.07

(A) Calculations for " K_1 " based on equation (70) (B) Calculations for $\frac{E_2}{E_1}$ K₂ based on equation (110) assuming $K_1 = 0.40$

a _"ideal" line was based on points at a high concentration of the styrene

b = "ideal" line was based on points at a low concentration of the styrene.

where " K_{\perp} " is the apparent value of K_{\perp} assuming equation (70) to be valid.

Assuming a K_1 value of 0.4, since at 350mA the K values from both constant styrene and anhydride approached each other, equation (110) was used to calculate the $\frac{E_2}{E_1}$ values shown in Table IV (A and B). When the p-methylstyrene concentration was maintained constant, the increase of the $\frac{E_2}{E_1}$ K₂ values with increasing wave length confirmed prior qualitative impressions.

The greater parabolic nature of the curves combined with the inevitable error in optical measurements did not allow the same consistent results when the anhydride was held constant. It will be noted in Table IV that when the available data was at high styrene molarities, the "K₁" values were generally low and $E_2 \frac{K_1}{K}$ values high. This is expected since only the 1:1² complex contributes at very low molarities.

C. QUANTITATIVE COMPARISON OF THE COMPLEXES AND PREDICTION OF OPTICAL DENSITY

The constants evaluated by the Interaction Theories are tabulated in Tables V, VI and VII along with an estimate of the average deviation in the experimental data for all wave lengths. The lower wave length limitation is always due to the increasing absorption of the anhydride.

The E_1K_1 and $E_2K_1K_2$ constants show good agreement within the experimental deviation between the constants derived from both theories I and II. (Tables V and VI).

The values of $E_2K_1K_2$ from Theory I in Table VII are not expected to have any quantitative meaning since K_1 has been shown to be significant. This would contradict the premises of the derivation of I. However, it has significance in that it indicates the increasing absorption of a second complex at higher wave lengths.

 $\frac{E_2}{E_1}$ K₂' in Table VII can be construed as a more quantitative measure of the interaction of the 1:1 complex of anhydride and p-methylstyrene with more anhydride, its validity depending on the validity of the presumed K₁. On the basis of this data, the following may be true.

(a) The 1:1 complex reacts separately with p-methylstyrene and maleic anhydride to form two additional and distinct 1:2 complexes.

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	TI	HEORY I	THEORY	II	
	E ₁ K	1	E2K1K2**		
MM	Anhydride Constant	Styrene* Constant	Anhydride Constant	ElKI	E2K1K2**
340	28 ±3			23 ±3	3.3 [±] 1
345				17 ± 1	1.17±0.25
3 50	14 ± 1	13.5±0.2		12.7±1	0.49±0.1
355	. .	6.8 ± 1		8.6±0.2	0.23±0.02
360	5.5 ± 0.3	5.7±0.3	0.14±0.05	5 .3±0.1	0.195±0.01
365		3.85±0.10	D	3.14±0.06	0.140±0.006
370	1.85±0.15	1.50±0.28	5 0.12 ± 0.02	1.77±0.06	0.110±0.007
375	1.03±0.10	0.97±0.1	5 0.09 ±0.0 2	0.92±0.05	0.084 [±] 0.005
380	0.56±0.09			0.51±0.02	0.047 ± 0.002
385				0.30±0.06	0.018±0.006
390				0.18 ± 0.01	0.007 ±0. 001
400					

* The estimated average deviations were based on
studies made at only two constant syrene concentrations.
** K₂ is the equilibrium constant for the interaction
of the l:l complex with styrene.

CONSTANTS FOR MALEIC ANHYDRIDE COMPLEXES WITH

STYRENE AS DETERMINED BY INTERACTION THEORIES I AND II

TABLE VI

	CONSTANTS FOR MALEIC ANHYDRIDE COMPLEXES				
WITH	H P-CHLOROS	TYRENES AS	DETERMINE	D BY INTERA	CTION
		THEORIE	S I AND II		
	THEORY	I		THEORY	II
_	E ₁ K1*	ElKI	E2K1K2**		
ми	Anhydride Constant	Styrene * Constant	Anhydride Constant	^E 1 ^K 1	^E 2 ^K 1 ^K 2 ^{**}
335	37 ±?				
340	30 ±?				
345	21 ± ?			19.3 ¹ 0.4	1.16±0.13
3 50	15.35 ±0.0 5	19 ± 2	0.644?	14.1 [‡] 0.3	0.93 ± 0.12
355	10.9±0.10	9.4 ± 0.3	0.7±0.3	9,8 ± 0,1	0.83 ±0. 06
360	7.3±0.3	6.5±0.7	0.7±0.1	6.7 1 0.4	0.64±0.20
365	5.13±0.05	5.13±0.09	0.58±0.02	4.5±0.2	0.50±0.14
370	3.57±0.04	3.64±0.13	0.36±0.1	3.0±0.15	0.40±0.05
375	2.40±0.01	2.54±0.10	0.26±0.03	2.1±0.13	0.281 ±0.015
380	1.62±0.04	1.64±0.08	0.17±0.07	1.42±0.12	.174±0.01
385	1.11±0.01		0.14±0.04	0994 ² 0005	0.122±0.001
390	0.82±0.05		0.12519	0.76±0.08	0.10±0.025
3 95	0.6±0.2		0.09 ± ?	0.50 ±0. 06	0.10±0.05
400	0.4±0.1		0.0561?	0.36 ± 0.04	0039 ±00 04
410	0.2±0.1		0.0461?	0.17 ± 0.02	002010004

* The estimated average deviations were based on studies made at only two constant concentrations.
** K₂ is the equilibrium constant for the interaction of the 1:1 complex with styrene.

TABLE VII

CONS	CONSTANTS FOR MALEIC ANHYDRIDE COMPLEXES WITH P-METHYL-				
STYR	ENE AS DET	ERMINED B	Y INTERACT	ION THEORIE	S I AND III
	Т	HEORY I		THEOR	Y III***
	E1 K1	E ₁ K ₁ *	B ₂ K ₁ K ₂ *	E ₂	E2 **
MM	Anhydride	Styrene [*]	Anhydride	E1 ² Anhydride	E1 Styrene
	Constant	Constant	Constant	Constant	Constant
330	109 ± 4				
33 5	96±3				
3 4 0	81 ± 2				
345	66 ±1				
350	53.6 [±] 0.5	53.3 ± 1.0			
355	41.4 ± 1.0	42.6 ± 0.5		0.202?	0.11=0.03
3 60	31.9 [±] 0.3	31.4±0.5		0.221?	0.20 ± 0.01
365	22.8±0.5	23.0±0.6			
370	16.6±0.3	16.4 ± 0.4		0.32±?	0.30 ±0. 00
375	11.3 [±] 0.3	11.340.5		0.33 ± ?	
380	7.31±0.06	7.8±0.4			
385	4.65±0.1		0.09±0.05		
390	3.08±0.04	3.11 ± 0.]	L		
400	1.07±0.08		0.05±0.05		
404	0.67±0.07				
410	0.38±0.07				
* K ₂ is the equilibrium constant for interaction of the					
1:1 complex with styrene.					
** K2' is the equilibrium constant for interaction of					
the 1:1 complex with anhydride.					
*** Based on assumed K1 = 0.4.					
**** Estimation of deviation is useless due to wide					
vari	variation in values obtained.				

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TABLE VIII

CONSTANTS* FOR MALEIC ANHYDRIDE COMPLEXES WITH P-METHOXYSTYRENE AND P-DIMETHYLAMINOSTYRENE

		17.T
mμ	P-METHOXYSTYRENE	P-DIMETHYLAMINOSTYRENE
3 50	137110	
3 6 0		277 ± 13
3 65		260 ± 26
375	72 ± 5	261 ± 22
400	32 * 2	236 ± 4
425		228 ± 1
450		197 ± 6
475		156 ± 1
500		100 *5
550		30.5 ±1. 5
600		4.8±0.3
65 0		2.0±0.1

EIKI

* These values are determined from zero-time (extrapolated) values with the postulate of a 1:1 complex. The average deviation includes results from studies at both constant anhydride and constant styrene concentrations.
(b) The 1:1 complex reacts with p-methylstyrene or anhydride to form a 1:2 complex which reacts further with the other reactant. A complex equilibrium is established between the three complexes.

Table IX is a summary of the constants from Theories I and II. These are weighted values compiled from Tables V, VI, VII and VIII.

Equation (104) can be rearranged to: (111)

$$D_{t} = \left[E_{1}K_{1} + E_{2}K_{1}K_{2}A_{0}\right] A_{0}B_{0}$$

or in our case

(112) $D_{t} = [E_1K_1 + E_2K_1K_2S_0] M_0S_0$

Thus, knowing the unreacted substituted styrene concentration (S₀) and the unreacted anhydride concentration (M₀) in benzene, the absorption of the formed complexes can be predicted using the E₁K₁ and E₂K₁K₂ values in Table IX appropriate to the wave length considered. In the p-methylstyrene complexes, the tabulated E₁K₁ alone suffices. The E₁K₁ value also serves as a good approximation with the p-methoxystyrene and p-dimethylaminostyrene complexes.

The smooth curves drawn on Figures 1 thru 6 were calculated from equation (112). The excellent agreement with the experimental points is the final proof of the reliability of the interaction theories as applied to these complexes.

Figure 2, Curve C, shows an unwarranted deviation. However, the dotted pair of points in Figure 14 fall

		TABLE	IX A				
SUMMARY	OF	CONSTANTS	FROM	THEORIES	I	AND	II
		E, I	ζ,				
		1	T				

mμ	R:	- H	-C1	-CH3	-OCH3	$-N(CH_3)_2$
330				109		
335			37	9 6		
340		25	30	81		
345		17	21	66		
350		13.3	14.9	53.5	137	
3 55		8.4	10.0	42.3		
360		5.3	7.0	31.8		277
365		3.2	5.1	22 .9		260
370		1.8	3.5	16.5		
375		0.95	2.4	11.3	72	261
380		0.52	1.6	7.4		
385		0.30	1.0	4.65		
390		0.18	0.8	3.09		
395			0.5	1.75		
400			0.4	1.07	3 2	236
404				0.67		
410			0.2	0.38		

* R is the para substituent of the styrene in the complex. off the plotted straight lines. This is some of the same data that comprise (2C)! This clearly shows that the predicted curve is even more valid than the experimental one in this instance.

Table IX shows the following additional facts: (a) The E_1K_1 and $E_2K_1K_2$ values for all complexes fall off toward the visible. The absorption curves of the complexes show no discernible maximum. A maximum may exist at shorter wave lengths but the absorption of the reactants makes this impossible to ascertain.

(b) The E_1K_1 ratios clearly show that the absorption of unsubstituted styrene complex falls off more rapidly toward the longer wave lengths than the p-chloro and p-methylstyrene complexes. The ratio between these latter two remain practically constant so that the contour of their absorption curves is similar. However, their absorptions decrease more rapidly than that of the complex with p-methoxystyrene which decreases more rapidly than that of the complex with p-dimethylaminostyrene.

These phenomena clearly show that a comparison of the optical densities of substituted styrene-anhydride mixtures at an arbitrary wave length is no criterion of complex concentrations or complex stability.

(c) Realizing that the error in these constants increases below 355 m/2 where the anhydride has appreciable absorption, the $\frac{E_2}{E_1} K_2$ values for the complexes with p-chlorostyrene and styrene are relatively constant for most wave lengths. This indicates that

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 E_1K_1 Ratios

mµ	H	:	Cl	:	CH3	:	OCH3	:	N(CH ₃) ₂
335	x		1.0		2.6		x		x
340	1.0		1.2		3.2		x		х
345	1.0		1.2		3.9		x		x
3 50	1.0		1.12		4.02		10.3		x
3 55	1.0		1.19		5.05		x		x
360	1.0		1.32		6.0		x		52 .3
365	1.0		1.59		7.17		x		81.3
370	1.0		1.94		9.18		x		x
375	1.0		2.53		11.9		76		275
380	1.0		3.08		14.22		x		x
385	1.0		3.33		15.5		x		x
390	1.0		4.44		17.17		x		x
39 5	x		1.0		3.5		x		x
400	x		1.0		2.7		80		600
404	x		x		1.0		x		x
410	x		1.0		1.9		x		x

E	2 ^K 1 ^K 2		E ₂ I Rat	⁽ 1 ^K 2 :ios		² 2
mµ R:	- H	-Cl	-H	: -Cl	- H	-Cl
340	3.30		l	x	0.13	
345	1.2	1.16	1	0.97	0.07	0.06
350	0.50	0.9	1	1.8	0.04	0.06
3 5 5	0.23	0.8	1	3.5	0.03	0.08
360	0.18	0.65	1	3.6	0.03	0.09
3 65	0.14	0.55	1	4.0	0.04	0.11
370	0.11	0.41	1	3.7	0.06	0.12
375	0.084	0.27	1	3.2	0.09	0.11
380	0.047	0.17	1	3.6	0.09	0.11
385	0.018	0.12	1	6.7	0.06	0.12
390	0.007	0.09	1	14.0	0.04	0.11

TABLE IX C

SUMMARY OF CONSTANTS FROM THEORIES I AND II

ratio of the absorption of the 1:2 complex (E_2) to that of the 1:1 (E_1) is relatively constant at all wave lengths. If we assume that the ratio E_2/E_1 is the same for both styrene complexes, then the stability of the p-chlorostyrene 1:2 complex is approximately twice that of the 1:2 complex with unsubstituted styrene.

It may be argued that the observed additional interaction with the substituted styrene is attributable to the gradual change of solvent, the styrene replacing benzene and since molarities were used instead of activities. These arguments may be refuted on several points.

1. The evaluated constants based on the theory allow calculated predictions to confirm experimental observations at all concentration ranges and wave lengths.

2. The relations between densities of benzene and the substituted styrenes show that there are less molecules of the styrenes per unit volume. This should be detrimental to interaction and not assist it. For a given molarity of anhydride there are proportionally less molecules of styrene in the more concentrated styrene solutions per given volume. The styrenes showed the same absorption as the benzene in the regions studied.

3. The choice of a benzene solvent is advantageous as no significant contractions in volume due to mixing of the hydrocarbons were evident. The complexing is thru the ethylenic linkages and the independent

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contributions of the aryl rings can probably be discounted except as they transfer the effect of the para substituent to the vinyl group. D. EFFECT OF DEOXYGENATION ON COMPLEX FORMATION

Application of equation (112) to p-methylstyreneanhydride mixtures prepared under nitrogen and described in the experimental section shows agreement between the calculated densities and those experimentally obtained. No effect of oxygen on complex formation and light absorption could be determined.

E. EFFECT OF DILUTION ON COMPLEX FORMATION

As stated in the experimental section, the optical densities were read on 0.05M maleic anhydride solutions with wide ranges of p-chlorostyrene and p-methylstyrene. Subsequent dilution of these solutions to 0.0250M anhydride showed their obedience to Beer's law and the law of mass action, denoting true equilibrium.(112) The Figures 10 and 13 show the respective curves.

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F. INTERPRETATION OF THE KINETICS: THE CHANGE IN OPTICAL DENSITY OF <u>COMPLEXES OF</u> P-DIMETHYLAMINOSTYRENE AND P-METHOXYSTYRENE

The optical density attributed to complex formation of p-dimethylaminostyrene and p-methoxystyrene with maleic anhydride changed with time.

In the latter case, the absorption was principally in the near ultraviolet region, and the observable density changes occurred so fast that extremely low concentrations had to be used. Absorption due to the styrene and the anhydride themseves interfered with a quantitative determination of the density of the complex and a true measure of its increase. The nature of the density changes were complex. These reasons made a quantitative application of kinetic theory infeasible with this complex.

However, the unique character of the density changes with p-dimethylaminostyrene warranted such a study.

1. The color of the formation (yellow-red) is pronounced and in the visible region where neither of the complex components absorb.

2. The initial complex, as determined by continuous variations on extrapolations to zero time, is definitely 1:1 and, even with the error concomitant









with such treatment, shows no clear evidence of other complexes. (See Figures 5 and 6.)

3. The magnitude of the equilibrium constant for the 1:1 complex is known. The nature of the kinetic curves provided positive clues as to the mathematics to be applied.

a. Figure (19) consists of two curves. Curve A shows the change in optical density for a mixture of equal volumes of p-dimethylaminostyrene and 0.25M maleic anhydride in benzene. Curve B is for a mixture of equal volumes of the 0.25M styrene and 0.25M anhydride. Notwithstanding the higher initial 1:1 complex concentration as evidenced by the initial optical densities, the absorption of Curve A shows a greater decrease than that of Curve B. Since 1:1 complex formation is an equilibrium phenomenon, the decrease in extinction shows that, at the very least, a reaction occurs between one part maleic anhydride and two or more parts of the styrene. Removal of the components in this ratio decreases the concentration of the 1:1 complex and thus the observed optical density.

b. Two solutions with the same total sum of reactant concentrations, (Figure 20) but each with one reactant in excess of the other, give kinetic curves of entirely different contours. Curve 20-A, with excess styrene, shows decreasing density that tends to level off at a much lower value than the initial.

Curve (20-B), with excess anhydride, initially

decreases in density, reaches a minimum and then increases at a faster rate which subsequently slows. The slowing in the optical density increase (Note arrow at curve 20-B) occurs simultaneously with an observed precipitation. The rate slows regardless of the increasing turbidity of the solution. With high excess of styrene (e.g. 20-A) no precipitation was ever observed.

These experimental observations are conclusive evidence of two kinetic reactions occurring either simultaneously or in sequence. One chemical entity is formed containing an excess of the styrene over that of the anhydride and has no (or less) absorption at the studied wave lengths than the 1:1 complex. Another may subsequently be formed by further reaction of this entity with anhydride or by simultaneous formation of a new chemical identity containing an excess of anhydride over that of the styrene. The former is the more probable however, as at all concentrations studied, an initial dip in density was always observable notwithstanding the high excesses of anhydride initially present. The subsequent heightening of the rate of density increase clearly demonstrates that the interaction with anhydride must be due to a reaction occurring subsequent to a former reaction with more styrene and not concomitantly.

No such phenomena could be discerned with separate solutions of the reactants in the benzene solvent.

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(t) time in thousands of seconds.

c. The greater the excess styrene concentration, the greater the tendency for an inverted "S" type curve with a good portion of the initial plot of the density (D) vs. time showing a definite linearity (Curve 21-A). Density decrease subsequently increased in rate which then diminished as noted above. Clearly a factor must be considered which affects the initial rate in such cases.

The above analyses served as clues for the theoretical kinetic investigation. It may be hypothesized that the initial linearity of the inverted "S" type curve may be due to 1:1 complex reacting with styrene and the equilibrium relationships necessitating the formation of additional 1:1 complex simultaneously with its removal. The further decrease in slope may possibly occur when all of the minor constituent (anhydride) is in the 1:1 complex and no more can be formed. The remainder of the curve may be investigated kinetically on an independent basis.

With a high excess of the styrene and a low concentration of the anhydride, the concentration of the 1:1 complex would be the determining factor in the kinetics. The reaction can be assumed to be first order with respect to the complex and so:

(113)

$$\frac{-dC_1}{dt} = k_1C_1$$

where C₁ is the concentration of the 1:1 complex.

But as complex (C₁) is consumed, the equilibrium creates more complex with the heretofore unreacted anhydride. The complex concentration is defined as: (114)

$$C_1 = K_1 SM = K_1 [S_0 M_0 - C_1 (M_0 S_0) + C_1^2]$$

where S_0 and M_0 are the respective concentrations of the styrene and anhydride if no 1:1 complex were formed.

Substituting (114) into (113), (115)

$$\frac{-d(K_1SM)}{dt} = \frac{-d(K_1S_0M_0)}{dt} + \frac{d(K_1C_1(M_0+S_0))}{dt} - \frac{d(K_1C_1^2)}{dt} = k_1C_1$$

M_o is presumed to be very small and (115) reduces to:

$$\frac{d(K_1C_1S_0)}{dt} - \frac{d(K_1C_1^2)}{dt} - K_1S_0\frac{dM_0}{dt} = k_1C_1$$

Expanding,

(117)

$$K_{1}S_{0}\frac{dC_{1}}{dt} + K_{1}C_{1}\frac{dS_{0}}{dt} - 2K_{1}C_{1}\frac{dC_{1}}{dt} - K_{1}S_{0}\frac{dM_{0}}{dt} = k_{1}C_{1}$$

 S_0 is initially very high so that very little change in its concentration occurs at the start of the reaction. Assuming S_0 equal to the original styrene concentration of the prepared mixture and constant, (118)

$$\frac{K_1 S_0 \frac{dC_1}{dt} - 2K_1 C_1 \frac{dC_1}{dt} - K_1 S_0 \frac{dM_0}{dt} = k_1 C_1}{dt}$$

To allow integration, an approximation is made that very small initial M_0 concentration is entirely tied up in the 1:1 complex, i.e. $M_0 = C_1$, and (119)

$$\frac{\mathrm{d}\mathrm{M}_{\mathrm{o}}}{\mathrm{d}\mathrm{t}} \cong \frac{\mathrm{d}\mathrm{C}_{\mathrm{l}}}{\mathrm{d}\mathrm{t}}$$

It follows from (118) that (120)

$$\frac{\mathrm{dC}_{1}}{\mathrm{dt}} = \frac{-\mathrm{k}_{1}}{2\mathrm{K}_{1}}$$

which integrates to

(121)

$$\frac{(c_1)_2 - (c_1)_1}{t_2 - t_1} = \frac{-k_1}{2K_1}$$

or since $\frac{D_1}{E_1} = C_1$

(122)

$$\frac{(D_1)_2 - (D_1)_1}{t_2 - t_1} = \frac{E_1 K_1}{2K_1}$$

For this substitution we have assumed that if $D_t = D_1 + D_2$ where D_2 is the density of the proposed 1:2 complex, the absorption due the second complex is initially small. This is valid as its extinction ,

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 (E_2) has already been shown to be low or nil and its initial concentration at the point considered is also low.

Thus the initial straight line portion of a plot of Density (D) vs. time (t) has a negative slope of $\frac{E_1K_1}{E_1E_1}$ and is of psuedo zero order.

2K1

Values of $E_{1}k_{1}$ are tabulated in Table X. Their constancy is $2K_{1}$ corroborative proof of the theory. The magnitude of k_{1} is 3 x 10⁻⁵ moles/l/sec. based on the assumed $K_{1} = 0.4$.

The reaction proceeds in this manner until the M₀ is completely consumed for all practical purposes. Since the decrease in density is no longer being retarded by the formation of new complex, the remainder of the density vs. time curve should be indicative of the kinetics of the reaction between the l:l complex and p-dimethylaminostyrene.

The rate of a reaction of the nth order is proportional to the nth power of the concentration of the reactant. Considering a high excess of p-dimethylaminostyrene we have:

(123)

$$\frac{-\mathrm{d}C_1}{\mathrm{d}t} = \mathbf{k}_1 C^n$$

and on integration:

$$\frac{c^{(1-n)}}{1-n} = -k_1 t+L$$

TABLE X

DETERMINATION OF FORWARD REACTION RATE CONSTANT

k,

P-DIMETHYLAMINOSTYRENE-MALEIC ANHYDRIDE

Initial Molarity of the Reactants

Mo	s _o	slope [#]	Moles/l/sec.**
0.015	0.639	2.2x10-4	2.7x10 ⁻⁵
0.020	0.547	2.3	2.9
0.0225	0.501	2.0	2.5
0.0238	0.479	1.7	2.1
0.025	0.456	1.9	2.4
0.0273	0.434	3.1	3.9
0.0275	0.411	2.7	3.4
0.0288	0.388	2.1	2.6
0.030	0.365	2.2	2.7
0.0325	0.319	1.4	1.8
0.0375	0.228	4.2	5.3

Average 2.3×10^{-4} 3 $\times 10^{-5}$ * slope = $\frac{E_1k_1}{2k_1}$ determined from slopes of initial $\frac{2k_1}{2k_1}$ straight lines of density plotted vs. time.

 $\frac{K_1}{K_1} \div K_1 = \frac{K_1}{K_1^2}$

 $E_1K_1 = 100$ (See Table VIII) at 500 m μ . For k_1 calculation, assumed $K_1 = 0.4$

KINETIC PLOTS OF P-DIMETHYLAMINOSTYRENE-MALEIC

ANHYDRIDE REACTION USING OPTICAL DENSITY (D) (500m)



seconds

where L is a constant of integration. Rearranging and taking logs:

(125) $\log C_1 = \frac{1}{1-n} \log t + \text{constant}$ or also (126) $\log D_1 = \frac{1}{1 - n} \log t + \text{constant}$

Log-log plots of density against time give a slop: of
$$1/1-n$$
. This method applied to the latter portion of the curves for the mixtures in Table X give an n ~ 1.3.

For higher concentrations of anhydride and for mixtures that show a mimimum density with a subsequent rise, values of n = 40 for the falling density portion have been calculated. With increasing anhydride, (n) increases, demonstrating the complexity of the kinetics.

Again considering high styrene concentrations and low anhydride concentrations, first order plottings of log density (D) vs. time (t) have decreasing negative slope. This indicates either that the observed density is greater than warranted by first order kinetics or the 1:1 complex is not consumed at the expected rate. (Figure 22-B) Second order plotting of 1/density (1/D) vs. time (t) shows an increasing slope. (See Curve 21-B) This confirms the intermediate order noted above. An estimate of the situation would be that the observed density is not decreasing at a fast enough rate to fully satisfy first order kinetics.

A reverse equilibrium may be postulated: 1:1 complex \rightarrow 1:2 complex.

Assume a first order reversible reaction (127) $SM + S \stackrel{\sim}{\leftarrow} S_2M$

(128) $c_1 + s \frac{k_1}{k_1} c_2$

With high concentrations of S, the reaction rate is first order with respect to C_1 . The rate expression is:

(129) $\frac{dC_2}{dt} = k (a-C_2) - k'C_2$

where (a) is the initial concentration of C₁ (no C₂ is present initially) and (k) and (k') are the respective specific rates for the forward and opposing reactions. At equilibrium

(130)
$$k(a-(C_2)_{\theta}) = k'(C_2)_{\theta}$$

where $(C_2)_{\theta}$ is the amount of C_2 formed or of C_1 changed to C_2 at equilibrium. Substituting the value of k' of (130) in (129): (131)

$$\frac{dC_2}{dt} = k(a-C_2) - \frac{k_1C_2}{(C_2)_{\theta}} \left[a - (C_2)_{\theta}\right] = \frac{k_1a}{(C_2)_{\theta}} \left[(C_2)_{\theta} - C_2\right]$$

On integration, $C_2 = 0$ at t = 0, $C_2 = C_2$ at t = t and (132)

$$\frac{ka}{(C_2)_{e}} = \frac{1}{(C_2)_{e}} \frac{\ln (C_2)_{e}}{(C_2)_{e}} - C_2$$
(133) $k + k' = \frac{ak}{(C_2)_{e}}$ and (132) is:

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(134) $k + k' = \frac{1}{t} \ln \frac{(C_2)_{\theta}}{(C_2)_{\theta} - C_2}$

but

$$(135) \qquad \frac{(C_2)_e}{(C_2)_e - C_2} = \frac{D_0 - D_e}{D_t - D_e}$$

where D_0 , D_t and D_u are the densities at the beginning, after time (t), and at equilibrium respectively, and so (136)

$$k + k' = \frac{1}{t} \int_{n} \frac{D_{0} - D_{\theta}}{D_{t} - D_{\theta}}$$

Rearranging:

(137)

$$(\mathbf{k}+\mathbf{k}')\mathbf{t} = -\ln (\mathbf{D}_{\mathbf{t}}-\mathbf{D}_{\mathbf{u}}) + \ln(\mathbf{D}_{\mathbf{0}}-\mathbf{D}_{\mathbf{u}})$$

If the hypotheses of this derivation are valid, a plot of the log (D_t-D_θ) vs. time (t) should have a negative slope $-\frac{k+k!}{2.303}$ and be a straight line.

Curve 22-A is one of a series of curves representative of the confirmation of the prediction. Such determined values of $k_1 + k$ are tabulated in Table XI. The value (D_e) is determined from the minimum of the density vs. time plot and the deviations from linearity depends on this choice.

As the initial styrene concentration is diminished, the overall forward reaction rate becomes second order with first order reversal. The rate expression is: (138)

 $\frac{\mathrm{d}C_2}{\mathrm{d}t} = \mathbf{k}(\mathbf{a}-\mathbf{C}_2)(\mathbf{b}-\mathbf{C}_2) - \mathbf{k}'\mathbf{C}_2$

where (b) is the initial concentration of uncomplexed styrene (S) and (a) is the original concentration of complex on the assumption that all the original anhydride (M_0) is contained within the 1:1 complex.

At equilibrium:

(139)

$$k(a-C_{e})(b-C_{e}) = k'C_{e}$$

and thus:

(140)

$$k' = \frac{k}{C_e} (a-C_e) (b-C_e)$$

where C_{Θ} is the concentration of C_2 at equilibrium since $C_2 = 0$ at the start of the reaction.

Substituting (140) in (138):

(141)

$$\frac{\mathrm{d}C_2}{\mathrm{d}t} = k(a-C_2)(b-C_2) - \frac{k}{C_2}(a-C_2)(b-C_2)C_2$$

Expanding and rearranging, this becomes:

(142)

$$\frac{dC_2}{(C_eC_2-ab)(C_2-C_e)} = \frac{k}{C_e} dt$$

Separating by the method of partial fractions, and setting up (142) for integration with limits as shown:

$$\frac{-C_{e}}{C_{e}^{2}-ab} \int_{0}^{C_{2}} \frac{dC_{2}}{C_{2}-ab} + \frac{1}{C_{e}^{2}-ab} \int_{0}^{C_{2}} \frac{dC_{2}}{C_{2}-c} = \frac{k}{C_{e}} \int_{0}^{dt} \frac{dC_{2}}{C_{e}} dt$$

Integrating and evaluating:

(144)

$$t = \frac{1}{k} \frac{C_e}{ab-C_e^2} \int_n \frac{C_e(ab-C_eC_2)}{ab(C_e-C_2)}$$

If (b) is large (i.e. original styrene concentration high), C_e^2 is small with respect to ab, (b) is practically constant and equation (144) reduces to (132), the first order forward reaction case. Thus at high styrene concentrations (b) the reaction is psuedo first order reversible as described, with k_p the apparent forward first order rate constant.

Comparison of equations (132) and (144) shows: (145)

$$t = -\frac{1}{k_{p}+k_{p}} l_{n}(C_{\theta}-C_{2}) + \frac{1}{k_{p}+k_{p}} l_{n}\left[C_{\theta}(1-\frac{C_{\theta}C_{2}}{ab})\right]$$

and if $\frac{C_eC_2}{ab}$ is small (145) can be converted into an equation analagous to (137) where: (146)

 $(k_p+k_p)t = -\ln(D_t-D_e) + \ln(D_0-D_e)$ Thus the negative slope of the plot log (D_t-D_e) vs. (t) divided by 2.303 of the above equation is: (147)

$$k_p + k_p' = \frac{kba}{C_e} + kC_e - ka \cong \frac{k_pa}{C_e} \cong kb + k'$$

It must be realized that these equations were considered on the basis of high styrene and very low anhydride concentrations. For the general case, the kinetic considerations lead to the complicated rate expression: (148)

$$\frac{dC_2}{dt} = kC_1 \left[S_0 - (C_1 + 2C_2) \right] - k'C_2 = kK_1 \left[M_0 - (C_1 + C_2) \right] \left[S_0 - (C_1 + 2C_2) \right]^2 - k'C_2$$

where S_0 and M_0 are the initial molarities of the styrene and anhydride before any complex formation, C_1 and C_2 are the concentrations of the 1:1 and 1:2 complex at any time (t) and K_1 is the equilibrium constant for the formation of the 1:1 complex.

Slight variations of high styrene concentrations at low anhydride concentrations may allow estimation of the second order forward rate constant (k) by means of equation (147).

The calculated values from the curves of the psuedo rate constants $k_p + k_p$ ' plotted against the initial styrene concentration (b) should give a straight line with (k) as the slope and (k') as the intercept. The values are tabulated in Table XI.

As the maleic anhydride concentration of the solution approaches that of the styrene the subsequent density increase after the minimum can only be caused by interaction with anhydride to form a chemical entity of higher extinction. The faster rate can only be justified on the subsequent interaction of anhydride with the 1:2 complex. The precipitation occurring concomitantly with the decrease in rate of density rise shows that the light absorbing material

TABLE XI	
P-DIMETHYLAMINOSTYRENE (S) AND MALEIC ANHYDRIDE	(M)
TABULATION OF APPARENT kptkp VALUES	
FOR REACTION OF 1:1 COMPLEXES WITH	

P-DIMETHYLAMINOSTYRENE

Initial Molarities of the Reactants		k _p + k _p '*
Mo	s _o	
0.0275	0.411	1.52 x 10 ⁻⁴
0.02625	0.434	1.88
0.02375	0.479	1.63
0.0225	0.501	1.63
0.020	0.547	1.78
0.015	0.639	1.86
	Average	1.7×10^{-4}

* Determined by dividing slope of plot of log (D_t-D_e) vs. time (t) by 2.303 according to equation (146)

Plotting $k_p + k_p$ ' vs. S₀ gives a straight line of positive slope according to equation (147), $k_p + k_p$ ' = k' + kS₀ From this plot $k = 1.9 \times 10^{-4}$, k' = 7. $\times 10^{-5}$

EFFECT OF EXCESS REACTANT

ON KINETICS OF P-METHOXYSTYRENE AND MALEIC ANHYDRIDE



is being removed from solution.

No matter how high the concentrations of p-methoxystyrene used with low anhydride concentration, no dip in optical density could be observed.

Figure 23 shows two curves at two extremes of the reactant concentration ratio: anhydride to p-methoxystyrene. No ultimate stabilization of optical density could be obtained even with very high p-methoxystyrene concentrations, in contrast to the p-dimethylaminostyrene. The divers mixtures studied always gave a precipitate and always showed increasing absorption. When precipitation started, a sharp decrease in optical density was noted approximately proportional to the amount of coagulant. (See arrow in Figure 23).

However, the initial rate of density increase was significantly slower than the subsequent rate when the styrene concentration was in excess. Conversely, with high concentration of anhydride the high initial rate of increase was subsequently lessened.

Interaction with a 1:1 complex may be hypothesized. An initial chemical entity with high p-methoxystyrene may be postulated as 1:2 on the basis of the well known alternating tendencies of the monomers in polymerization. This entity has a lower extinction than any others that are formed simultaneously since the slower the increase in density, the greater the relative p-methoxystyrene concentration. However, other entities are simultaneously formed, as is evidenced by the initial high increase of absorption with high anhydride. It is reasonable to postulate that a 2:1 complex of the initially absorbing material (1:1) with another molecule of anhydride is formed concomitantly. The subsequent increased rate of density rise can be attributed to a series of complex reactions between the various complexes establishing chromophores. The precipitation removes these chromophores from solution and the density decreases at a rate qualitatively estimated as being proportional to the rate of decrease in observed optical density.

The immediate interaction with greater anhydride and its pronounced effect on absorption is indicated by the asymetry of the continuous variation curves in Figure 4.

G. CORRELATION OF THE OBSERVED KINETICS WITH STRUCTURE AND ALTERNATING TENDENCIES IN COPOLYMERIZATION

The kinetics of interaction between p-dimethylaminostyrene and maleic anhydride can be explained on the basis of instantaneous (1:1) complex formation, its subsequent reaction with a molecule of the styrene followed by reaction with the anhydride.

Certain substituents (p-dimethylamino and p-methoxy) result in a distinctive polarity and high resonance stabilization^{15,21} of the 1:1 complex. The complex so stabilized tends to have subsequent selective reaction with more of the styrene.

This 1:2 complex is not an observable chromophore and its paramagnetic properties may be substantially reduced. The achievement of a constant low optical density in the p-dimethylaminostyrene case suggests that the 1:2 complex is the only one present with residual 1:1. It may be stable and hence isolable. Reaction of the 1:2 complex with maleic anhydride if sufficient is present subsequently occurs and is probably accompanied by other heterogenous reactions between complexes. Very low molecular weight polymers were indicated. With p-methoxystyrene, the kinetic curves indicate that there is a simultaneous interaction of 1:1 complex with both anhydride and the styrene.

The high alternation of p-dimethylaminostyrene and p-methoxystyrene can now be correlated with observed kinetic phenomena. The exceptionally great alternating tendency observed in their copolymers is consistent with kinetically observed selectivity. Furthermore, the more complete alternation in the copolymer of maleic anhydride with p-dimethylaminostyrene could be predicted on the basis of its kinetically observed selectivity.

The fact that styrene, p-methylstyrene and p-chlorostyrene when reacted with maleic anhydride do not give rise to changing absorption with time clearly shows that a different mechanism must be postulated for the two groups of styrene in contrast to the overall theory developed by Mayo et al¹⁵.

H. RESULTS OF INFRA RED STUDIES

No clarification in the infra red spectra of styrene-maleic anhydride complexes was obtainable with available equipment. Calculation of complex extinction values by subtracting the extinction values of the styrene and anhydride was based on recorded transmission curves. The error was sufficient to account for most deviations. There is a slight indication, however, of increased conjugated aromaticity by a very slight shift in the absorption maximum corresponding to this property of the styrene.

SUMMARY

The method of continuous variations proves the
 existence of instantaneously formed 1:1 complexes
 (substituted styrenes with maleic anhydride) and
 indicates additional complexes.

2. Generally applicable theories have been developed to prove the simultaneous existence and composition of several complexes in solution when the method of continuous variations fails.

3. These methods have been applied to the complexes studied.

4. Constants have been evaluated allowing the prediction of the optical density of such complexes at all wave lengths.

5. The existence of true equilibrium and the adherence to Beer's law for the 1:1 complexes has been demonstrated. This equilibrium is established instantaneously.

6. Comparison of solutions of the same concentration in the substituted styrene and anhydride to spectrophotometrically compare complex stability is not warranted.

7. The kinetics of the interaction of p-dimethylaminostyrene and p-methoxystyrene with maleic anhydride have been studied and interpreted. It has been shown that other complexes are formed.

8. The observed kinetics have been correlated with structure and alternating tendencies in copolymerization.
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