

TABLE VI

Model	Non-equilibrium cases	$\Gamma = \frac{\text{Actual rate}}{\text{equilibrium rate}}$	Amount of reaction, %	Time, sec.
$k_{13} = k_{14} = k_{41} = k_{42} = 0.001$ $k_{23} = k_{32} = k_{24} = k_{31} = 0.1$ $k_{12} = k_{43} = 0.01$ $k_{21} = k_{34} = 1$	Case II: $A_1 = D/2.02$ $A_2 = A_3 = A_4 = 0$	0.80	0.87	1
1)				
$k_{13} = k_{31} = k_{24} = k_{42} = k_{14} = k_{41} = 0$ $k_{23} = k_{32} = k_{21} = k_{34} = 1$ $k_{12} = k_{43} = 0.01$	Case I: $A_1 = D/1.01$ $A_2 = (D/1.01) \times 10^{-2}$ $A_3 = A_4 = 0$.67	.87	2
	Case II: $A_1 = D/1.01$ $A_2 = A_3 = A_4 = 0$.65	.90	3
2)				
$k_{13} = k_{31} = k_{24} = k_{42} = k_{14} = k_{41} = 0$ $k_{23} = k_{32} = 0.1$ $k_{21} = k_{34} = 1$ $k_{12} = k_{43} = 0.01$	Case I: $A_1 = D/1.01$ $A_2 = (D/1.01) \times 10^{-2}$ $A_3 = A_4 = 0$.918	.87	10

Our modified model (1) of the four-level system especially for the Case II of non-equilibrium is in every respect analogous to the problem of simultaneous chemical reactions. The end species A_1 and A_4 are the stable reactant and product, respectively, whereas A_2 and A_3 are the unstable concentrations. This case is an addition to similar ones treated by A. Skrabal¹¹ in his series of papers on the subject of simultaneous chemical reactions. This treatment applies directly to unimolecular reactions with or without an inert gas and to bimolecular or higher order reactions where one reactant is in much lower concentration than the others. Other cases which lead to non-linear equations provide special mathematical difficulties, but the results would be similar.

(11) A. Skrabal, *Monatsh.*, **24**, 293 (1943), and earlier papers.

Summary

The results obtained taking into consideration the quantized nature of molecular energy levels in testing the applicability of the equilibrium theory of absolute rates of reaction are essentially in agreement with the results found by H. A. Kramers. The general procedure employed complements the classical diffusion approach to this problem. Further application of this treatment to more complicated systems ($n > 4$) is deemed necessary in order to indicate what refinements are to be made in the theories of reaction rates. The first author wishes to acknowledge his appreciation of the privileges extended to him by the University of Utah where the greater part of this research was carried out.

PRINCETON, N. J.

RECEIVED APRIL 11, 1947

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Ultraviolet Absorption Spectra of Substituted Vinyl Aromatic Monomers and Polymers¹

BY H. A. LAITINEN, FOIL A. MILLER AND T. D. PARKS²

In applying the ultraviolet absorption method of Meehan³ to the analysis of copolymers of butadiene with various substituted styrenes and other aromatic vinyl type monomers, it was necessary to obtain the absorption spectra of the polymers of each of the monomers for calibration purposes. Since the absorption maxima most useful for analytical purposes lie in the wave length range 250–300 $m\mu$, the data were restricted to this region.

(1) This investigation was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government Synthetic Rubber Program.

(2) Present address: Shell Development Company, Emeryville, California.

(3) E. J. Meehan, *J. Polymer Sci.*, **1**, 175 (1946).

Absorption data were also collected for some of the monomers in the same wave length range, inasmuch as it was necessary to prove the complete removal of monomers from the polymers and copolymers. A small amount of residual monomer would lead to a large error because of its relatively intense absorption.

Experimental

The freshly distilled monomers, synthesized by the Organic Division,⁴ were polymerized in bulk by irradiation with ultraviolet light. A 1 to 2 ml. sample of monomer in

(4) C. S. Marvel, *et al.*, *THIS JOURNAL*, **67**, 2250 (1945); **68**, 786, 861, 1085, 1088 (1946); R. L. Frank, *et al.*, *ibid.*, **68**, 1365, 1368 (1946).

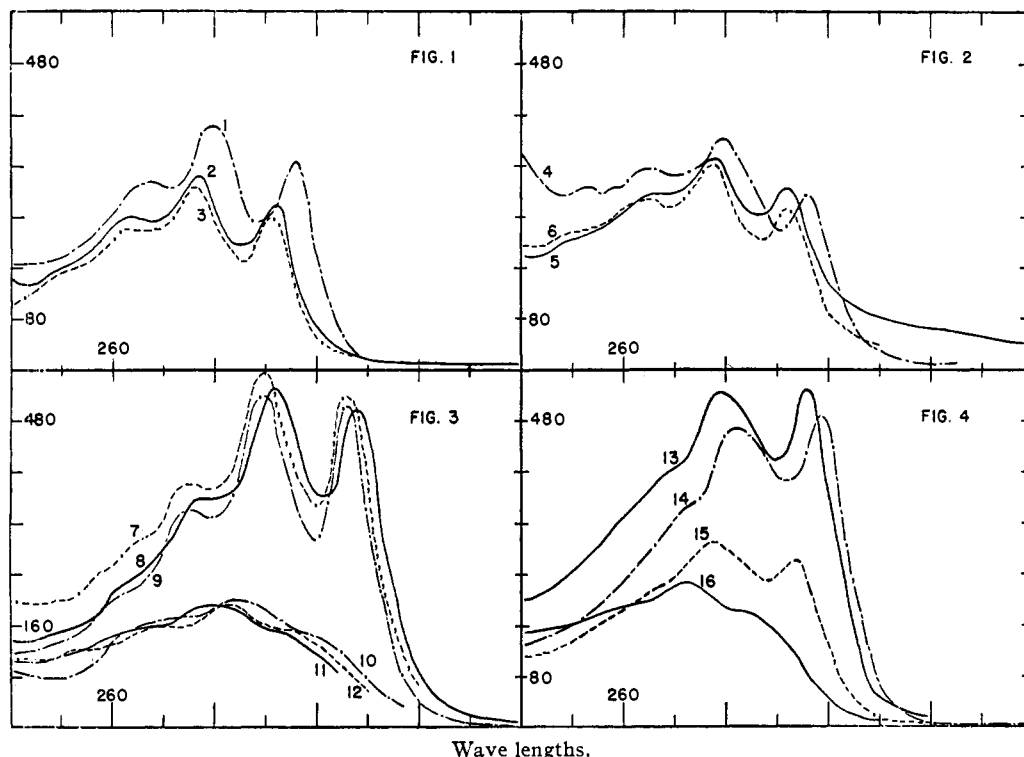


Plate I.—Figures 1–4.—The wave lengths along the abscissa axes are marked at intervals of 5 $m\mu$. Ordinates are molecular extinctions (ϵ). The curves are for polymers of: (1) *p*-chlorostyrene, (2) *m*-chlorostyrene, (3) *o*-chlorostyrene, (4) *p*-bromostyrene, (5) *o*-bromostyrene, (6) *m*-bromostyrene, (7) 3,4-dichlorostyrene, (8) 2,5-dichlorostyrene, (9) 2,4-dichlorostyrene, (10) 2,3-dichlorostyrene, (11) 2,6-dichlorostyrene, (12) 3,5-dichlorostyrene, (13) 2,4-dimethylstyrene, (14) 2,5-dimethylstyrene, (15) 3,4-dimethylstyrene, (16) 3,5-dimethylstyrene.

a Pyrex test-tube was exposed for twenty-four to seventy-two hours to the radiation of a Hanovia mercury arc until most of the monomer had undergone polymerization as evidenced by its greatly increasing viscosity. Anethole, which did not polymerize under these conditions, was polymerized in toluene solution at room temperature using stannic chloride as a catalyst.

To remove the residual monomers, the polymers were dissolved in chloroform and precipitated by the addition of methanol. A three-fold precipitation was found generally effective in removing the last traces of monomer, except in the case of 2-vinyl-5-ethylpyridine, which was most effectively removed from its polymer by Soxhlet extraction with aqueous hydrochloric acid.

Accurately weighed samples which had been dried in a vacuum desiccator at 60° were dissolved in chloroform and diluted until the maximum optical density of the solution was in the range 0.4 to 1.0.

Absorption measurements were made with a Beckman Model DU Quartz Spectrophotometer using chloroform as the comparison solvent in matched 1-cm. quartz cells.

Results

From the optical density of the solution, $D = \log_{10}(I_0/I)$, which was read directly from the instrument, the specific extinction coefficient E was calculated by the relation $E = D/cl$, where c is the concentration in g. per liter and l is the cell length.

To compare various polymers on an equimolecular monomer basis, the molecular extinction ϵ

was calculated for the polymers from the relation $\epsilon = ME$, where M is the molecular weight of the monomer unit. The usual definition of molecular extinction would have no significance for high polymers of unknown molecular weight. However Smakula⁵ has shown that the specific extinction coefficients of polystyrene at its absorption maxima are independent of the molecular weight of the polymer. Hence it is justifiable to consider each monomer unit of the polymer as an absorbing unit, and to calculate molecular extinction values on the basis of this monomeric unit.

The absorption curves of the polymers are shown in Plates I and II, and those of the monomers in Plate III. It will be noted that the monomer curves are plots of specific rather than molecular extinction coefficients. The positions of the most important maxima are shown, and a comparison of the intensities of the maxima is made in Table I for the polymers and Table II for monomers.

The ultraviolet spectrum afforded a convenient means of determining the monomer ratio in various copolymers. For example the amount of *p*-chlorostyrene in a copolymer with butadiene as measured by this method agreed well with the

(5) A. Smakula, *Angew. Chem.*, **47**, 777 (1934).

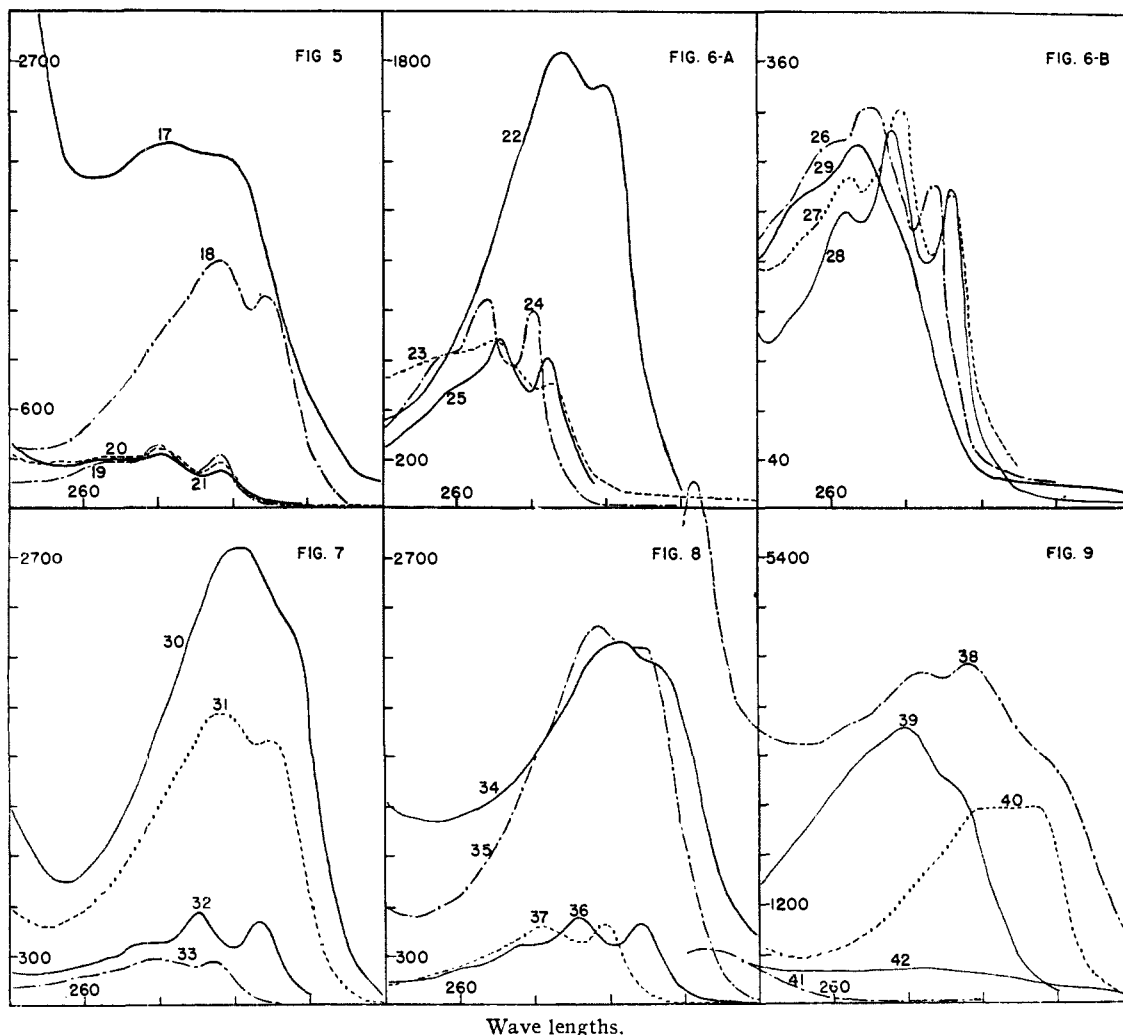


Plate II.—Figures 5–9.—The wave lengths along the abscissa axes are marked at intervals at 10 μ . Ordinates are molecular extinctions (ϵ). The curves are for polymers of: (17) *p*-phenoxy styrene, (18) anethole, (19) *p*-chlorostyrene, (20) *p*-bromostyrene, (21) *p*-cyanostyrene, (22) *m*-methoxystyrene, (23) *m-s*-butylstyrene, (24) *m*-fluorostyrene, (25) *m*-trifluoromethylstyrene, (26) *m*-methylstyrene, (27) *m*-bromostyrene, (28) *m*-chlorostyrene, (29) *m-l*-butylstyrene, (30) 3,4-dimethoxystyrene, (31) 3-methyl-4-methoxystyrene, (32) 3,4-dichlorostyrene, (33) 3,4-dimethylstyrene, (34) 2-methoxy-5-methylstyrene, (35) 2-methoxy-5-*t*-butylstyrene, (36) 2,5-dichlorostyrene, (37) 2,5-dimethylstyrene, (38) β -vinyl naphthalene, (39) 2-vinyl-5-ethylpyridine, (40) 2-methyl-4-methoxy-5-isopropylstyrene, (41) α -vinyl thiophene, (42) α -vinyl furan.

results obtained by analyzing the copolymer for chlorine.⁶

Discussion

It seems worth while to point out that some order can be brought to the spectra of the various polystyrenes reported here. Polystyrene itself consists of saturated hydrocarbon chains substituted by phenyl groups, $[-CH(Ph)-CH_2-]_x$. The absorptions which are observed in the neighborhood of 2700 Å. are to be attributed to these phenyl groups, since benzene has an absorption

band in this region whereas saturated hydrocarbons exhibit no electronic absorption above 2000 Å. These phenyl groups are always separated by at least two saturated carbon atoms which act as very effective insulators against electron transfer. Consequently the electronic energy levels of one phenyl group are almost completely unaffected by the presence of a neighboring phenyl group. Hence as far as the near ultraviolet spectrum is concerned, one may equally well regard polystyrene as an assembly of substituted and practically independent benzene molecules.⁷ Šklar

(6) E. J. Meehan, T. D. Parks and H. A. Laitinen, *J. Polymer Sci.*, **1**, 247 (1946).

(7) Smakula's findings (ref. 5) are a logical consequence of this concept.

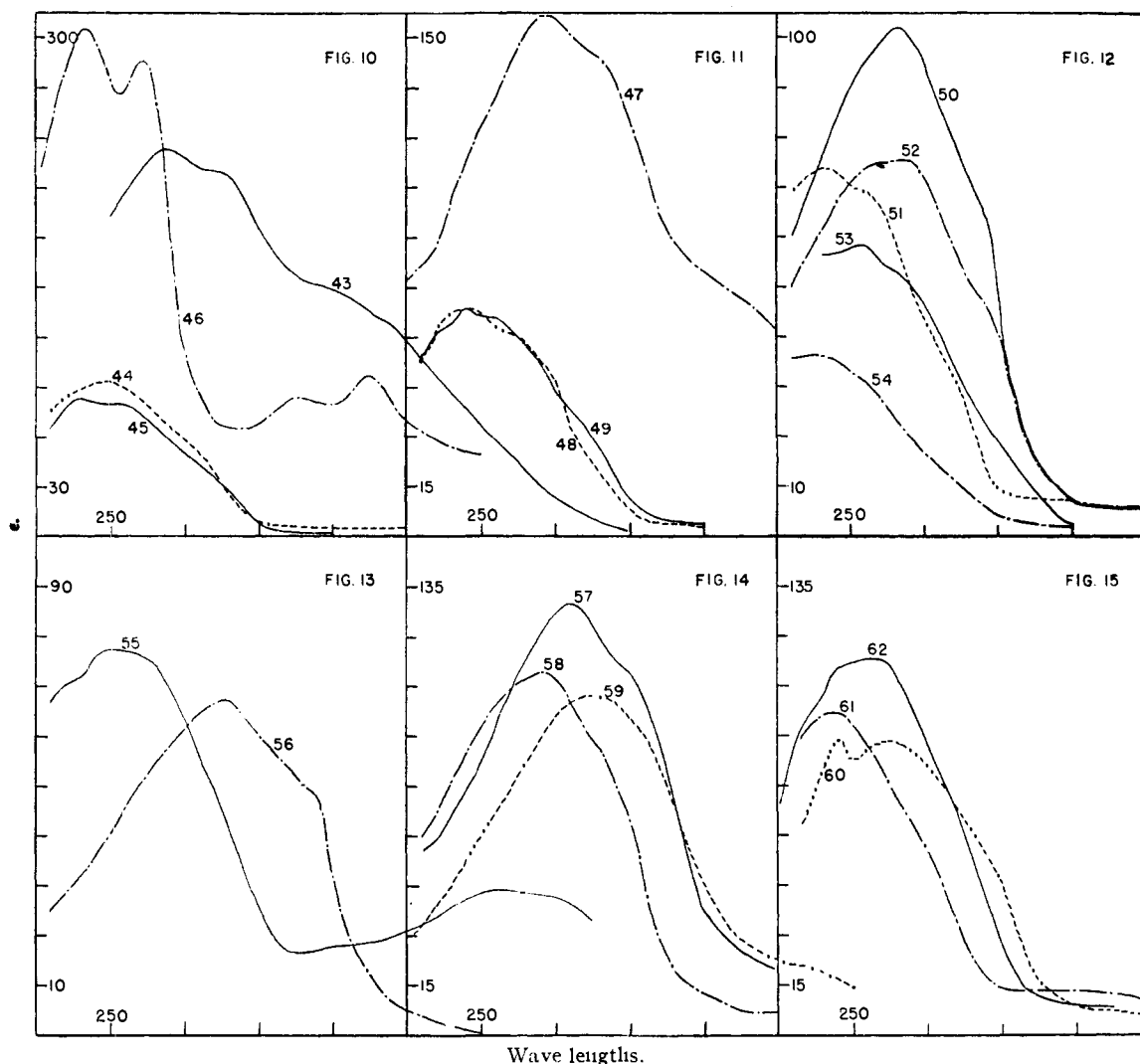


Plate III.—Figures 10–15.—The wave lengths along the abscissa axes are marked at intervals of 10 μ . Ordinates are specific extinctions (E). The curves are for monomers of: (43) *p*-chlorostyrene, (44) *m*-chlorostyrene, (45) *o*-chlorostyrene, (46) β -vinylnaphthalene, (47) *p*-bromostyrene, (48) *m*-bromostyrene, (49) *o*-bromostyrene, (50) 3,4-dichlorostyrene, (51) 2,5-dichlorostyrene, (52) 2,4-dichlorostyrene, (53) 2,3-dichlorostyrene, (54) 2,6-dichlorostyrene, (55) 2-methoxy-5-methylstyrene, (56) α -vinylfuran, (57) anethole, (58) *p*-cyanostyrene, (59) 3-methyl-4-methoxystyrene, (60) 3,5-dimethylstyrene, (61) *m*-fluorostyrene, (62) *m*-methylstyrene.

has made a theoretical study of the intensities of electronic absorption in substituted benzenes.^{8a,b,c} We shall briefly summarize his theory and then apply it qualitatively to our data.

The 2700 Å. transition in benzene itself is forbidden electronically. Hence if the molecule were held rigidly to its planar hexagonal symmetry, the absorption would not appear. Its actual observance can be attributed to the existence of vibrations which lower the symmetry. This may be termed a "vibrational" effect and the intensity due to it designated I_v .

(8) (a) A. L. Sklar, *J. Chem. Phys.*, **7**, 984 (1939); (b) *ibid.*, **10**, 135 (1942); (c) *Rev. Mod. Phys.*, **14**, 232 (1942).

Consider now a substituted benzene. The substitution destroys the 6-fold electronic symmetry of the ring, because in general the substituent causes electrons to migrate into the ring (*ortho-para* directing group) or to migrate away from the ring (*meta* directing group). The 2700 Å. transition is then no longer forbidden electronically. This has been termed a "migrational" effect, and the intensity due to it may be designated I_m . There will also be a vibrational contribution to the intensity similar to that in unsubstituted benzene, and the total intensity of the transition is the sum of the two: $I = I_m + I_v$. Sklar's theory treats only the migrational inten-

TABLE I
 ABSORPTION MAXIMA OF THE POLYMERS

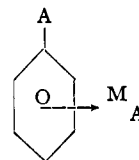
Fig.	Curve	Polymer	$m\mu_{\max}$		E_{\max}		ϵ_{\max}		
			1st	2nd	1st	2nd	1st	2nd	
1	1	Poly- <i>p</i> -chlorostyrene	270	278	2.75	2.35	381	326	
	2	Poly- <i>m</i> -chlorostyrene	268	276	2.20	1.86	305	258	
	3	Poly- <i>o</i> -chlorostyrene	268	276	2.09	1.71	290	237	
2	4	Poly- <i>p</i> -bromostyrene	270	278	1.98	1.51	362	276	
	5	Poly- <i>o</i> -bromostyrene	269	276	1.81	1.56	331	286	
	6	Poly- <i>m</i> -bromostyrene	269	276	1.76	1.39	322	254	
3	7	Poly-3,4-dichlorostyrene	275	283	3.20	3.00	554	519	
	8	Poly-2,5-dichlorostyrene	276	284	3.08	2.87	533	497	
	9	Poly-2,4-dichlorostyrene	275	283	3.00	2.90	519	502	
	10	Poly-2,3-dichlorostyrene	270	...	1.11	...	192	..	
	11	Poly-2,6-dichlorostyrene	272	...	1.15	...	199	..	
4	12	Poly-3,5-dichlorostyrene	272	...	1.10	...	190	..	
	13	Poly-2,4-dimethylstyrene	270	278	3.95	4.01	522	530	
	14	Poly-2,5-dimethylstyrene	271	279.5	3.55	3.69	469	488	
	15	Poly-3,4-dimethylstyrene	268.5	277	2.17	1.97	287	260	
	16	Poly-3,5-dimethylstyrene	266	...	1.71	...	226	..	
	5	17	Poly- <i>p</i> -phenoxystyrene	272.5	...	11.31	...	2220	..
		18	Polyanethole	278	284	10.11	8.65	1500	1280
19		Poly- <i>p</i> -chlorostyrene	270	278	2.75	2.35	381	326	
6a	20	Poly- <i>p</i> -bromostyrene	270	278	1.98	1.51	362	276	
	21	Poly- <i>p</i> -cyanostyrene	270	278	2.52	1.83	325	236	
	22	Poly- <i>m</i> -methoxystyrene	274	280	13.70	12.65	1840	1695	
	23	Poly- <i>m-s</i> -butylstyrene	265	273	4.23	3.15	678	505	
6b	24	Poly- <i>m</i> -fluorostyrene	264	270	6.94	6.54	848	799	
	25	Poly- <i>m</i> -trifluoromethylstyrene	265	272	3.96	3.56	682	613	
	26	Poly- <i>m</i> -methylstyrene	266	274	2.72	2.21	321	261	
	27	Poly- <i>m</i> -bromostyrene	269	276	1.76	1.39	322	254	
	28	Poly- <i>m</i> -chlorostyrene	268	276	2.20	1.86	305	258	
	29	Poly- <i>m-t</i> -butylstyrene	263	...	1.84	...	295	..	
	30	Poly-3,4-dimethoxystyrene	281	...	16.82	...	2760	..	
7	31	Poly-3-methyl-4-methoxystyrene	278	284.5	11.85	10.81	1755	1600	
	32	Poly-3,4-dichlorostyrene	275	283	3.20	3.00	554	519	
	33	Poly-3,4-dimethylstyrene	268.5	277	2.17	1.97	287	260	
	34	Poly-2-methoxy-5-methylstyrene	282	...	14.80	...	2195	..	
8	35	Poly-2-methoxy-5- <i>t</i> -butylstyrene	279	...	11.99	...	2280	..	
	36	Poly-2,5-dichlorostyrene	276	284	3.08	2.87	533	497	
	37	Poly-2,5-dimethylstyrene	271	279.5	3.55	3.69	469	488	
	38	Poly- β -vinylnaphthalene	272	278	25.9	26.6	3995	4100	
9	39	Poly-2-vinyl-5-ethylpyridine	270	...	24.95	...	3325	..	
	40	Poly-2-methyl-4-methoxy-5-isopropylstyrene	281	286	12.41	12.55	2360	2390	
	41	Poly- α -vinylthiophene	243	...	6.12	...	674	..	
	42	Poly- α -vinylfuran	270	...	4.50	...	423	..	

sity. The vibrational contribution cannot be predicted, and in our case data are not available for evaluating it empirically.

In determining I_m , two restrictions are laid on the substituent groups. First, they are to possess no absorption of their own near or above 2600 Å. (thus eliminating $-\text{NO}_2$, $-\text{COOH}$, $-\text{CHO}$). Second, they are not to exhibit large migrational effects. In chemical terms, this means that they are not to be strongly-directing on further substitution of the benzene ring. This eliminates the OH and NH_2 groups among others.

In monosubstituted benzene there will be a transition moment M due to the migrational effect. Sklar has shown that this moment will lie

in the plane of the ring, but at right angles to the ring-substituent bond.



If now a second substituent is introduced into the ring, it too will contribute a transition moment due to the migration of its electrons. These two moments may be added vectorially. The total migrational intensity of absorption (I_m) is proportional to the square of this resultant transition

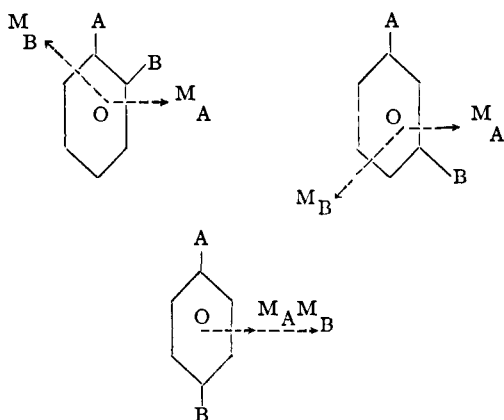
TABLE II
 ABSORPTION MAXIMA OF THE MONOMERS

Fig. Curve	Monomer	$m\mu_{\max}$	E_{\max}
10 43	<i>p</i> -Chlorostyrene	258	233
44	<i>m</i> -Chlorostyrene	250	94.5
45	<i>o</i> -Chlorostyrene	246.5	83.5
46	β -Vinyl-naphthalene	247	308
11 47	<i>p</i> -Bromostyrene	259	156
48	<i>m</i> -Bromostyrene	248	69.4
49	<i>o</i> -Bromostyrene	248	68.6
12 50	3,4-Dichlorostyrene	257	102
51	2,5-Dichlorostyrene	246	73.8
52	2,4-Dichlorostyrene	257	75.9
53	2,3-Dichlorostyrene	252	58.5
54	2,6-Dichlorostyrene	244	36.7
13 55	2-Methoxy-5-methylstyrene	250	78.2
56	α -Vinylfuran	266	67.5
14 57	Anethole	262	130
58	<i>p</i> -Cyanostyrene	258	111
59	3-Methyl-4-methoxystyrene	265	103
15 60	3,5-Dimethylstyrene	248	89.0
		255	89.0
61	<i>m</i> -Fluorostyrene	248	97.0
62	<i>m</i> -Methylstyrene	253.5	113

moment. Obviously both the direction and the phase of the second vector with respect to the first are important. These are given by the following two theorems.

Theorem I.—If there are two *para*-directing (or two *meta*-directing) substituents on a benzene ring which are separated by the angle $\tau = \angle AOB$, the migrational moment due to the second substituent is displaced from that due to the first by the angle τ and is multiplied by $(-1)^{3\tau/\pi}$.

Thus for *ortho*, *meta* and *para* substitution the transition moments have the relative orientations



If the two substituents are identical it is readily seen that the migrational intensities are in the ratio: monosubstituted: *ortho*: *meta*: *para* = 1:1:1:4.

Theorem II.—The transition moment of a *meta*-directing radical is 180° out of phase from the moment of a *para*-directing group located at the same position in the ring.

These theorems may be extended to any number of substituents. The vectors due to the various substituents are added together to obtain the resultant transition moment vector, and the square of this resultant is proportional to the migrational intensity. The total intensity is obtained by adding to this the vibrational intensity (which we shall not be able to evaluate).

This total intensity is equal to the oscillator strength in the vapor phase, which can be calculated from measurements on a solution by means of the equation⁹

$$f = \left(\frac{3}{n_0^2 + 2} \right)^2 \frac{2300 \, n c^2 m}{N \pi e^2} \int \epsilon d\nu$$

where

- f = oscillator strength of vapor
- n_0 = refractive index of solvent at ν
- n = refractive index of solution
- c = velocity of light
- m = mass of electron
- e = charge on electron
- N = Avogadro's number
- ν = wave number (cm.^{-1})
- ϵ = molecular extinction coefficient = $(1/C) \log_{10}(I_0/I)$
- C = concentration in moles/liter
- l = length of absorbing path in cm.

The integration is to be carried out over the entire width of the electronic band.

Because we shall be able to predict relative values for only a part of the total intensity (*i. e.*, only for I_m), it is convenient to make the following simplifications. (1) The area under the ϵ versus wave number curve will serve almost as well as the oscillator strength for comparing intensities, inasmuch as the index of refraction does not vary greatly from sample to sample. (2) The area under the ϵ versus wave length curve can be used for a less reliable comparison of the intensities. This is possible because all the absorption bands are in the same region of the spectrum (250–290 $m\mu$), with the absorption peaks at very nearly the same wave lengths. The data have been presented in this form because it seems to be the most convenient for analytical purposes. (3) For a very crude measure of intensity, the value of the extinction coefficient at the peak of the absorption curve is useful.

We now proceed to compare observed intensities in several series of polystyrenes. Within each series all the members possess the same ring substituents, but the positions of substitution differ. Two remarks are in order. (1) Since the masses and the force constants of the substituent groups are the same for all members of a series, one might expect that the vibrational contributions to the total intensity would be roughly the same.^{5b} The order of increasing intensity would then be determined largely by the order of the migrational intensity, which is just the order that can be predicted. (2) The hydrocarbon chain of the polymer, which is one of the substituents on each ring,

(9) Reference 8c; see also N. Chako, *J. Chem. Phys.*, **2**, 644 (1934); R. S. Mulliken, *ibid.*, **7**, 14 (1939)

has a nearly identical effect on the absorption of each phenyl group in spite of its variable structure. The effect is very nearly the same as that which would be produced by substituting an isopropyl group in the same position in every case.

The first series to which we apply these arguments is that of the polymonochlorostyrenes. Using Theorem I, one would predict the intensities to be as follows: $p\text{-Cl} > m\text{-Cl} \approx o\text{-Cl}$. The observed results are shown in Fig. 1 and in Table I-1. In the table the polymers are arranged in the order of decreasing area under the ϵ vs. wave length curve. It is seen that the predictions are verified. The same order would be expected for the poly-monobromostyrenes: $p\text{-Br} > m\text{-Br} \approx o\text{-Br}$. Figure 2 and Table I-2 summarize the data. Again the order is as predicted, although in this case the difference between the intensities of the para compound and the others is not large.

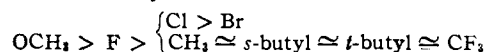
Going now to the tri-substituted benzenes, we consider first the complete series of polydichlorostyrenes. The predicted order of decreasing intensities is: poly-2,4-dichlorostyrene \approx 2,5 \approx 3,4 $>$ 2,3 \approx 2,6 \approx 3,5. Figure 3 and Table I-3 furnish striking confirmation. The same relative order is expected for the polydimethylstyrenes, of which four members are available. Figure 4 and Table I-4 show that this is found, although the break between the strongly- and weakly-absorbing members is not as clear-cut as in the dichloro series.

One can also predict the relative intensities of absorption of two polymers which are substituted at the same ring positions by different groups. That group having the greater tendency to move electrons toward or away from the ring will have the greater migrational moment. This tendency for electron transfer has been divided into the inductive, inductomeric, electromeric and mesomeric effects. Various groups have been arranged in the order in which they exhibit these effects,¹⁰ but the effects frequently oppose each other and it is not always easy to decide which will be the most important. A further complication is the fact that the vibrational contributions to the total intensity can no longer be assumed to be approximately the same from polymer to polymer. Consequently even if the predicted order of migrational intensity is correct, it may not always agree with the observed order of total intensity. In spite of these difficulties one can make a fairly successful estimate of relative intensities, especially if the migrational moments are clearly of different magnitudes.

The first series to be considered consists of poly-*p*-bromo, -*p*-chloro and -*p*-cyanostyrene. To these may be added the polymer of anethole, $[-\text{CH}(p\text{-C}_6\text{H}_4\text{OCH}_3)-\text{CH}(\text{CH}_3)-]_n$, since the β -methyl group will have only a negligible influence. Ordering first the *para* directing groups, one would predict the intensities to be $\text{OCH}_3 >$

$\text{Cl} > \text{Br}$. The cyanide group is *meta* directing, and according to Theorem II its migrational moment will be partially canceled by that of the hydrocarbon chain. Hence this polymer is expected to have the weakest absorption. Finally, the polymer of *p*-phenoxystyrene may be included in the series. The phenoxy group can act as either a good electron source or an electron sink, so this derivative should have the most intense absorption of all. The complete prediction then is: $\text{OC}_6\text{H}_5 > \text{OCH}_3 > \text{Cl} > \text{Br} > \text{CN}$. The observed results in Fig. 5 and in Table I-5 are in agreement.

Data are also at hand for the following series of *meta* substituted polystyrenes: F, Cl, Br, CF_3 , CH_3 , *s*-butyl, *t*-butyl, OCH_3 . The estimated order of intensity is



Figures 6a and 6b and Table I-6 contain the experimental results. In this case there is little agreement between prediction and observation.

Another example is that of the poly-3,4-disubstituted styrenes: -3,4-dimethoxy, -3-methyl-4-methoxy, -3,4-dichloro, and -3,4-dimethyl. According to Theorem I all the substituents make a positive contribution toward the resultant migration moment vector. This resultant, and therefore the intensity, is predicted to decrease in the order in which the polymers are listed, with the reservation that the last two may be inverted. Figure 7 and Table I-7 show that the original order is followed.

Finally there are four poly-2,5-disubstituted styrenes whose intensities are expected to decrease in the order -2-methoxy-5-methyl $>$ -2-methoxy-5-*t*-butyl $>$ -2,5-dichloro $>$ -2,5-dimethylstyrene. There is a possibility that the first two or the last two may be inverted. Figure 8 and Table I-8 show that the original order is correct.

For the remaining polymers (Fig. 9), no interpretation has been attempted.

In the case of the monomers one of the substituents is the vinyl group. One might expect that Sklar's theory would no longer be applicable because the π electrons of the vinyl group may interact strongly with those of the ring. The theory was not designed to fit cases of strong interaction. Nevertheless the predictions are at least qualitatively fulfilled.¹¹ The vinyl group is *ortho-para* directing,¹² and therefore intensities of the chlorostyrenes are predicted to be: *p*-chlorostyrene $>$ *m*-chlorostyrene \approx *o*-chlorostyrene. This is nicely verified in Fig. 10. The same result is found for the bromostyrenes (Fig. 11). And finally the intensities of the dichlorostyrene monomers are in the predicted order with the 2,4-, 2,5- and 3,4- dichloro isomers having the strongest absorption (Fig. 12).

(11) The cyanide group, which also contains π electrons, has been found by Sklar to fit the theory both qualitatively and quantitatively; see reference 8b.

(12) D. L. Hammick and W. S. Illingworth, *J. Chem. Soc.*, 2358 (1930).

(10) A. E. Remick, "Electronic Interpretations of Organic Chemistry," John Wiley and Sons, New York, N. Y., 1943, pp. 58-68.

The remaining series of monomers are so incomplete that the data are presented (Figs. 13-15) without any attempt at correlation.

Summary

1. The ultraviolet absorption of the monomers and polymers of a number of substituted vinyl aromatic compounds are reported for the range 250-300 $m\mu$.

2. The ultraviolet absorption method has been successfully applied to the determination of the monomer ratio in copolymers of butadiene with many of these substituted vinyl aromatic compounds.

3. The relative intensities of absorption for various substituted polystyrenes have been compared with predictions based on a theory by Sklar.

URBANA, ILLINOIS

RECEIVED MARCH 20, 1947

[CONTRIBUTION FROM THE RESEARCH LABORATORIES, PARKE, DAVIS AND CO.]

The Ultraviolet Absorption Spectra of Simple Unsaturated Compounds. I. Mono- and *p*-Disubstituted Benzene Derivatives

BY LEONARD DOUB AND J. M. VANDENBELT

Benzene exhibits absorption in two regions of the accessible ultraviolet. One is a highly resolved band of low intensity (ϵ max. = *ca.* 200) at 240-60 $m\mu$. The other is an intense band (ϵ max. = 7,400) in the neighborhood of 200 $m\mu$. The majority of studies reported in the literature have been concerned with the longer wave length absorption and have assumed that absorption of benzene derivatives in this region is best explained by modification of this band. That the shorter wave length high intensity absorption might be displaced in derivatives to account for spectra near 250 $m\mu$ has been recognized in at least one instance.¹ Surprisingly, however, there appears to have been no systematic study of the fate of this band in simple benzene derivatives although numerous isolated reports of high intensity short wave length absorption are on record.²⁻⁸ Clearly it is of importance for the rationalization of the effect of substitution on benzene absorption to relate the maxima of a given derivative to one or the other of these parent bands and to discriminate from effects following the introduction of new chromophoric groups.

This study of the effect of substitution on the short wave length (*ca.* 200 $m\mu$) absorption of benzene in general corroborates and extends the concept that this band is capable of displacement to and beyond 250 $m\mu$. In addition, it would appear to provide a basis for a more logical inter-

pretation of benzenoid absorption than has heretofore appeared.

Methods and Materials.—A Beckman quartz spectrophotometer with a hydrogen discharge tube source was used for all measurements. Extinction coefficients were calculated by dividing the observed densities by the molar cell concentration. Dilutions were prepared such that the peak absorption of each band fell on the density scale between 0.4 and 0.8. Readings in the difficulty accessible region below 220 $m\mu$ were obtained so far as possible at a slit width of 1.0 mm.; if necessary the check switch position at 0.1 was used.

Calibration of the instrument with a mercury vapor arc indicated that the wave length scale in the ultraviolet region was correct to a few tenths of a millimicron. Reported wave lengths of band peaks are therefore taken directly from the highest instrument readings as the peak was read through in small increments; in the case of a broad band the center was estimated by symmetry from its graph.

Liquids were redistilled before use. Solid compounds were recrystallized from a suitable solvent. Boiling and melting points were checked with the literature values as a confirmation of purity. Liquid samples such as benzene and toluene were weighed into stoppered flasks and dissolved in methanol. This solution was diluted into water and a blank containing the same amount of methanol prepared for instrument reading. The methanol concentration was never greater than 2%.

General Absorption Characteristics.—Figure 1 gives curves of representative monosubstituted and *p*-disubstituted derivatives.⁹ The curves

(1) Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 151.

(2) Dede and Rosenberg, *Ber.*, **67**, 147 (1934).

(3) Flexser, Hammett and Dingwall, *THIS JOURNAL*, **57**, 2103 (1935).

(4) Morton and McGoekin, *J. Chem. Soc.*, 901 (1934).

(5) Conrad-Billroth, *Z. physik. Chem.*, **B19**, 76 (1932); **B20**, 222 (1933); **B25**, 139 (1934); **B25**, 217 (1934).

(6) Kumler and Strait, *THIS JOURNAL*, **65**, 2349 (1943).

(7) Kumler, *ibid.*, **68**, 1184 (1946).

(8) The above are a few representative studies on short wave length benzenoid absorption. The following sources may be consulted for others: "International Critical Tables," Vol. V, McGraw-Hill Book Co., Inc., New York, N. Y., 1929; Morton, "Absorption Spectra," 2nd ed., Adam Hilger, London, 1942; Brode, "Chemical Spectroscopy," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1943.

(9) The absorption spectra of the majority of the compounds contained in this study have been reported previously at least in part. These have been repeated and recorded here because most of the earlier curves are unreliable in the range below 220-230 $m\mu$ or are not reported at all in this region. In addition, the diversity of solvents used in these previous studies renders comparison extremely difficult. In this study the solvent is water, except in those few cases where a trace of methanol was used to facilitate solution of the compound. Water was chosen as the solvent because the conditions