ments are purely statistical, and not influenced by any perceptible energy differences. The similarity of the values in different solvents would have the same significance. The small differences which are observed could be attributed to differences in the entropy of entanglement, entanglements being slightly more probable in chlorobenzene, for example. A lower intrinsic viscosity, reflecting a greater tendency for the polymer chain to coil back on itself, should be associated with a greater entanglement probability[18] and hence a higher rigidity, in agreement with Table IV.

The network hypothesis predicts that the rigidity should be independent of molecular weight, provided the latter is high enough so that free ends outside entanglements can be neglected. Data are not yet available to test this conclusion.

From mechanical measurements at much higher frequencies on undiluted polyisobutylenes of low molecular weight, Mason and Baker[19] have also postulated an elastic mechanism involving twisting of the polymer chains.

Interpretation of Model Constants.—If $\tilde{G}$ (Table VI) represents the hindered rotation elasticity mechanism, η_S could represent relaxation by rotation over the barriers or by slippage at entanglement points. Probably both mechanisms should occur, in different frequency ranges. According to Kuhn,[17] the former should be represented by a single relaxation time, directly proportional to the number of bonds involved; for the network, then, the relaxation time should be inversely proportional to concentration, and η_S should be proportional to c^2. This appears to be the case for the chlorobenzene solutions. However, measurements should be extended to a broader frequency range before a detailed interpretation is attempted.

Summary

1. The propagation of transverse waves in solutions of polyisobutylene ($\bar{M}_\eta$ = 1,200,000) in *n*-heptane, xylene, isoöctane, and chlorobenzene has been studied as a function of frequency, temperature, and concentration.

2. The rigidity $\tilde{G}$ increases only slightly with frequency in the range from 100 to 1000 cycles/sec.

3. At constant weight concentration, $\tilde{G}$ decreases slightly with increasing temperature; at constant volume concentration (c), $\tilde{G}$ is independent of temperature.

4. The rigidity is proportional to c^3; in the different solvents, the ratio $\tilde{G}/c^3$ increases slightly in the order named above, which is also the order of decreasing intrinsic viscosities (at 20°).

5. The damping index, λ/x_0, decreases with increasing frequency or passes through a minimum.

6. The dispersion of rigidity and damping in chlorobenzene solutions can be fitted by a retarded Maxwell element with a ratio of parallel to series viscosity of 0.013.

7. The concentration dependence of $\tilde{G}$ can be interpreted in terms of a transient network structure with storage of elastic energy by twist against potentials opposing free rotation about bonds in the chains.

MADISON, WISCONSIN RECEIVED AUGUST 30, 1948

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[18] A lower intrinsic viscosity means that in very dilute solution a smaller volume is pervaded by the average polymer coil. In concentrated solution, also, the volume pervaded is probably smaller. In concentrated solution, however, the domain of each coil is thoroughly interlaced by other molecules. The number of entanglements per cc. should be practically independent of the size of coil domain; but it should be markedly influenced by local chain configuration, back kinking giving rise to "snagging," and hence higher entanglement probability.

[19] W. P. Mason, W. O. Baker, H. J. McSkimin and J. H. Heiss, *Phys. Rev.*, **73**, 1074 (1948).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Variation of Monomer Pressure with Degree of Conversion in Emulsion Polymerization of Butadiene and of Butadiene–Styrene[1]

BY E. J. MEEHAN

Introduction

During a polymerization reaction the pressure of the unpolymerized monomer decreases as the reaction proceeds to completion. The way in which the pressure changes with the degree of conversion of monomer to polymer depends upon the monomer and upon the nature of the polymerization system. Different relations between pressure and conversion are observed in a homogeneous system (solution or bulk polymerization) and in a heterogeneous system (emulsion polymerization).

Pressure measurements can yield certain information about the nature of the polymerization system. Thus in a homogeneous system pressure measurements gave directly the value of the monomer activity in the thermal polymerization of pure styrene.[1a] In the emulsion polymerization of a monomer which is only slightly soluble in water, the unreacted monomer is present as a separate (oil) phase during the earlier part of the reaction; in the latter part of the reaction the unre-

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[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.

[1a] Walling, Briggs and Mayo, THIS JOURNAL, **68**, 1145 (1946).

acted monomer is entirely dissolved in the polymer particles. The pressure of the system evidently indicates the exact point at which the separate monomer phase disappears. It was shown by W. B. Reynolds[2] that the pressure of butadiene remains constant and equal to the vapor pressure of pure butadiene during more than the first half of the emulsion polymerization of butadiene, corresponding to the presence of a separate phase of butadiene. The disappearance of this phase is made evident by an abrupt decrease of the pressure from that of pure butadiene. As another example the application to copolymerization studies may be mentioned. The pressure of a copolymerizing system is related to the composition of the copolymer which is formed. The pressure may increase, remain unchanged, or decrease during the first part of the reaction, depending on whether the copolymer contains less than, the same amount as, or more than, the relative amount of the more volatile monomer present at the beginning of the reaction.

It is possible to give a simple interpretation of the data of a copolymerizing system only so long as the oil phase is present. After this phase has disappeared one is dealing with a solution of excess of monomers in a suspension of polymer. If the monomer–polymer system were ideal in the sense that the partial pressure of the monomer would be proportional to the mole fraction of the monomer, there would be no significant decrease in pressure until the consumption of monomer had become substantially complete. Thus in the conversion of a monomer of molecular weight 100 into a polymer of number-average molecular weight 40,000, the mole fraction of unreacted monomer in the monomer–polymer system is 0.99 at 80% conversion and is 0.80 at 99% conversion. Actually a marked decrease in pressure occurs at conversions smaller than 80%, because polymer–solvent systems do not follow Raoult's law; the entropy of mixing is very different from the entropy of mixing given by classical thermodynamics.

In this paper data are given showing the dependence of pressure upon conversion in the emulsion polymerization of butadiene and of butadiene–styrene mixtures. The points of principal interest were the disappearance of the monomer phase in both cases and the connection with copolymer composition in the latter case. A discussion of data obtained after the disappearance of the oil phase is not given at the present time.

Experimental

A. Preparation of Polymerization Charges

The following formula was used in the preparation of the charges: temperature, 50 or 30°

Ingredient	Parts by weight
Monomer(s)[a]	100
Water	180
Soap	Variable[b]
Potassium persulfate	0.3
n-Dodecylmercaptan	0.5

[a] Either butadiene or butadiene (75)–styrene (25). [b] Usually 5; otherwise varied from 10 to $^5/_8$.

The sources and purities of the various ingredients were the same as in previous investigations.[3] The charges were prepared either in 4-ounce glass bottles with metal screwcaps lined with self-sealing gasket material obtained from Dr. E. A. Willson of the B. F. Goodrich Company, or in a special metal reaction vessel described in a later section.

B. Pressure Measurements

1. Use of Pressure Gages.—Some measurements were made using ordinary pressure gages by the method described by Harrison and Meincke.[4] The charges were prepared in glass bottles, and the pressure was measured by removing the bottle from the 50° thermostat and inserting through the self-sealing gasket a pressure gage equipped with a hypodermic needle. To minimize loss of butadiene from the bottle during this operation, the gage was maintained at a temperature of about 51° and the pressure in the gage was maintained at a pressure approximately equal to or greater than that expected in the bottle. The precision of these pressure measurements is about 2 pounds per square inch.

2. Manometric Measurements.—Houston and Briggs at Goodrich[5] constructed a mercury manometer of sufficient height to permit measurement on butadiene-containing systems at 50°, and determined pressure–conversion relations for a number of comonomer systems. A mercury manometer of similar dimensions was constructed in this Laboratory and used in connection with a completely closed polymerization system. The polymerizations were carried out in a chromium plated vessel with a capacity of about 100 ml. The vessel, subjected to horizontal agitation, was connected to the manometer system by means of a flexible brass helix leading to an iron vessel which served as mercury reservoir for the open-end manometer. Both helix and reservoir were immersed in the thermostat; this prevented the distillation of butadiene from the reaction vessel at 50° into the manometer. Since the mercury well was about one meter above the lowest point of the manometer it was possible to read pressures lower than atmospheric pressure.

In use, the polymerization vessel was filled with the ingredients of the charge and sealed. It was connected to the helix after the helix and the air space in the mercury well had been pumped out and flushed with butadiene several times to remove the last trace of oxygen. The pressure was read to the nearest millimeter during the desired period of time. At the end of the experiment hydroquinone was injected and the conversion was determined by the usual method of total solids. The pressures reported correspond to mm. at room temperature rather than at 0°. The over-all accuracy of the measurements was estimated to be better than 0.5%.

Results

A. Monomers and Monomer Mixtures.—Accurate values of the vapor pressure and other thermal properties of pure 1,3-butadiene have been given by the Bureau of Standards.[6] The vapor pressure found at 50° was 4264 mm. (corrected to a column of mercury at 0°), and the rate of change of vapor pressure with temperature at 50° was 112 mm. per degree (calculated from the empirical pressure–temperature equation).

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[2] W. B. Reynolds, private communication, March, 1944.

[3] E. J. Meehan, *J. Polymer Science*, **1**, 175 (1946).

[4] S. A. Harrison and E. R. Meincke, *Anal. Chem.*, **20**, 47 (1948).

[5] R. J. Houston and R. A. Briggs, private communication, Nov. 1, 1945.

[6] R. B. Scott, C. H. Meyers, R. D. Rands, Jr., F. G. Brickwedde and N. Bekkedahl, *J. Res. Nat. Bur. Standards*, **35**, 39 (1945).

The vapor pressure of butadiene at 50° was found in this research to be 4.27 meters with an average deviation of about 0.01 meter. This value agrees well with that of the Bureau of Standards; the precision of 0.01 meter indicates that the temperature was controlled within about 0.1°. Accurate values of the vapor pressure of styrene have been given by Pitzer, Guttman and Westrum[7] who found the vapor pressure at 50° to be 24.23 mm. mercury. The vapor pressure of styrene has been measured also by Patnode and Schreiber.[8] From the empirical equation given by these authors, one calculates that at 50°, $p = 24.4$ mm.

Known mixtures of butadiene and styrene of mole fraction of butadiene ranging from 1.000 to 0.278 were prepared in the metal vessel by adding a known amount of styrene by pipet, followed by the addition of slightly more than the desired weight of butadiene, which had been liquefied in Dry Ice–acetone. The excess of butadiene was allowed to evaporate until the desired weight was present, and the vessel was then quickly sealed. (The amount of styrene which evaporates with the excess of butadiene is negligibly small.) The observed pressures of the mixtures were found to agree within experimental error with the values calculated from the pressures of the pure monomers on the assumption that they form an ideal solution.

B. Vapor Pressure of Polymerizing Systems

1. Pressure Variation During the Emulsion Polymerization of Butadiene.—It was shown already by Reynolds[2] that the pressure remained constant during the first (approximately) 60% conversion in the emulsion polymerization of butadiene. The experiments described now were directed to establish whether or not the conversion at which the butadiene pressure first becomes less than the pressure of pure butadiene depends on the amount of soap initially present in the charge. Charges were prepared according to the previously quoted recipe with the amount of soap varied from 10 ("2 soap") to 5/8 ("1/8 soap"). The results of the pressure and conversion determinations are given in Table I.

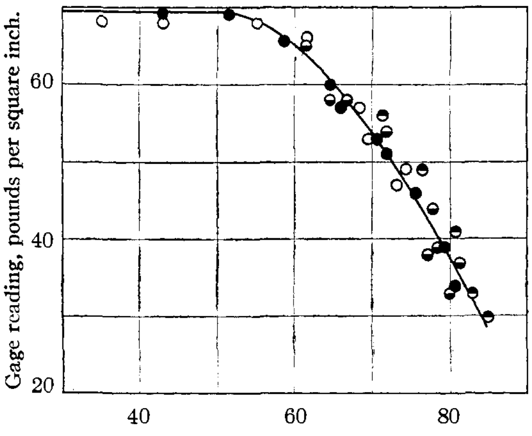

Fig. 1.—Emulsion polymerization of butadiene at 50°: ●, 2X soap; ⊖, 1X soap; ◓, 1/4X soap; ○, 1/8X soap.

TABLE I

RELATION BETWEEN PRESSURE AND CONVERSION IN THE EMULSION POLYMERIZATION OF BUTADIENE AT 50°: 100 BUTADIENE, 180 WATER, 0.5 DDM, 0.3 PERSULFATE, AND S. F. FLAKES AS INDICATED

Time in hr.	Gage pressure, pounds per sq. in.	Conv., %	Gage pressure, pounds per sq. in.	Conv., %
		A. 2 Soap		
6	..	..	69	45.4
7	..	..	69	51.9
8	..	..	66	58.4
9	57	65.9	60	64.7
10	51	71.7	53	70.4
11	46	75.4	..	..
12	39	79.3	..	..
13	34	80.5	..	..
		B. 1 Soap		
13	64	..	..	..
13.5	..	..	65	61.6
14	64	..	..	..
15	62	..	58	66.8
16	58	64.6	54	71.6
17	53	69.5	49	..
18	..		44	77.7
18.25	47	..	..	..
19	..	..	39	78.7
20	38	77.1	37	81.1
21	33	80		
		C. 1/4 Soap		
10	68	..		
15	68	..		
22	56	71.3		
24	48	76.4		
26	41	80.7		
28	33	83.0		
30	30	85.1		
		D. 1/8 Soap		
26	68	..		
31	68	55.1		
33	66	61.5		
35	57	68.3		
37	49	74.2		

The data of Table I are plotted as Fig. 1. It appears that the butadiene pressure first decreases at about 52% conversion, regardless of the amount of soap (from 2X to 5/8X) initially present in the charge. The size of the polymer particles in the latex is changed greatly as the soap content is varied sixteen-fold. Thus it appears that the amount of butadiene which can dissolve in the polymer particles is determined only by the amount

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(7) K. S. Pitzer, L. Guttman and E. F. Westrum, Jr., THIS JOURNAL, **68**, 2209 (1946).

(8) W. Patnode and W. J. Schreiber, *ibid.*, **61**, 3449 (1939).

of polymer and not by the size of the polymer particles.

This conclusion depends upon the assumption that an equilibrium value of the solubility is attained and maintained during the reaction. This was proved to be so in the following way. In several experiments the polymerization was halted (short-stopped) at various conversions greater and smaller than 52%, by the injection of hydroquinone. The pressure subsequently did not change upon continued rotation at 50° for twenty-four hours.

In a similar way (pressure gage technique) the pressure was determined during the emulsion polymerization of butadiene at 30°. It was found that the pressure drop occurred at the same conversion (52%) as at 50°, thus indicating that the solubility of butadiene in polybutadiene is not markedly temperature-dependent.

A few experiments were made with the accurate manometric technique with polybutadiene at 50° to verify the conclusions reached above on the basis of the gage measurements. In polymerizations with 1× and with $^1/_4\times$ the ordinary amount of soap (5 parts per 100 parts monomers), it was found that the pressure drop occurred between 51–52% conversion.

2. Variation of Pressure in the Emulsion Copolymerization of Butadiene–Styrene.—The composition of the copolymer formed in the emulsion copolymerization of butadiene–styrene varies during the reaction.[9] The polymer initially formed contains relatively more butadiene than is present in the charge, so that the proportion of butadiene in the residual monomers decreases during the reaction. This causes a continual decrease in the pressure of the system apart from the relatively abrupt decrease which is observed when the separate phase of residual monomers disappears.

The variation of pressure with conversion up to about 60% conversion was determined accurately in two separate experiments for the previously-quoted mixture with 75 parts of butadiene, 25 parts of styrene and 5 parts of soap. The experiments were made by observing the pressure as a a function of time, and determining the conversion at the end of the experiment. The conversion at a given time could be calculated since it had been established that the rate of conversion in this recipe is constant up to more than 60% conversion. It was not attempted to adjust the weight of butadiene added to the reaction vessel to exactly the correct figure; moreover, some butadiene is lost in the operation of flushing out the manometer system to remove air. For these reasons the initial pressures observed in the experiments did not correspond exactly to that expected for a mixture containing 75.0% butadiene. Therefore all the observed pressures (after subtraction of 92 mm., corresponding to the vapor pressure of water at 50°) were corrected to an initial butadiene content of 75.0%, by multiplying all the values by the ratio of the theoretical initial pressure to the observed initial pressure. The data, corrected as described above, are given in Table II and Fig. 2.

TABLE II

VARIATION OF MONOMER PRESSURE WITH CONVERSION IN THE EMULSION COPOLYMERIZATION OF BUTADIENE (75)–STYRENE (25) AT 50°

Experiment A		Experiment B	
Conversion, %	Pressure,[a] mm.	Conversion, %	Pressure,[a] mm.
0	3650	0	3650
7.9	3641	3.5	3646
9.1	3641	6.9	3641
13.8	3637	13.8	3636
24.3	3620	25.9	3616
39.5	3586	34.6	3590
45.9	3546	41.6	3565
47.1	3527	48.4	3521
48.8	3506	50.4	3494
50.6	3487	50.9	3491
51.8	3464	51.6	3480
52.9	3431	55.1	3414
53.6	3424	57.0	3393
54.1	3406	62.6	3213
		63.1	3199

[a] Adjusted to the theoretical initial pressure of 3650 mm. Hg.

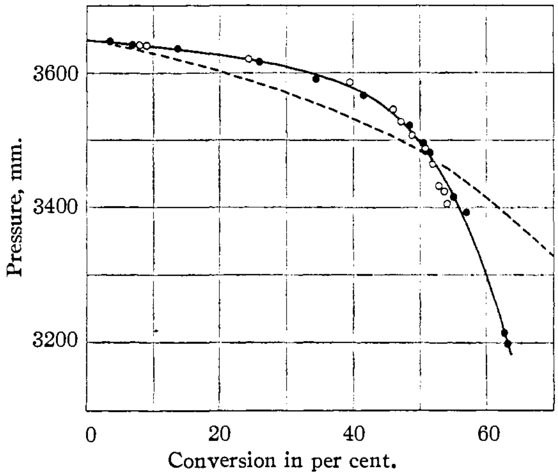

Fig. 2.—Pressure–conversion curve: emulsion polymerization of butadiene (75)–styrene (25), 50°.

Since the composition of the copolymer is known as a function of conversion[9] it is possible to calculate the composition of the total residual monomers at any conversion. Thus if a copolymer containing 19.2% styrene is formed at 50% conversion from a mixture which contained originally 75% butadiene, the residual monomers evidently contain 69.2% butadiene. This calculation does not give any information about the composition of the oil phase, since the residual monomers are in part dissolved in the polymer. So if the two monomers are dissolved to different extents in the

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(9) E. J. Meehan, *J. Polymer Science*, **1**, 318 (1946).

polymer, the distribution would result in a difference in the composition of the monomer mixture in the two phases.

If it is assumed (the correctness of the assumption can be checked immediately) that the composition of the free monomer phase is the same as that of the total monomer mixture, the dependence of pressure upon conversion can be calculated solely from the copolymer composition and the vapor pressures of the pure monomers, since the monomers form an ideal solution. The values so calculated are compared with the observed values in Fig. 2.

From Fig. 2 it is seen that up to about 50% conversion the observed and calculated pressures are in excellent agreement, the maximum deviation being less than 1.3%. The observed pressure becomes markedly less than the calculated value around 52% conversion, which indicates that it is at, or somewhere before, this conversion that the monomer phase disappears by solution in the polymer.

The point at which the monomer phase disappears also was determined approximately by visual examination of non-polymerizing systems. A quantity of "stripped" GR-S latex (*i. e.*, latex from which nearly all the unreacted monomers had been removed) of 69.3% conversion was obtained through the courtesy of Mr. W. K. Taft of the Government Rubber Pilot Plant in Akron, Ohio. To a definite amount of this latex of known polymer content, was added, in an ordinary polymerization bottle, such an amount of butadiene and styrene that the mixture polymer—monomer would correspond to 45, 50, 55 or 60% conversion. (For example, to prepare a latex corresponding to 55% conversion, 45 g. of mixed monomers was added to a quantity of latex which contained 55 g. of polymer.) The composition of the monomer mixture added to the latex was calculated by stoichiometry from the composition of the copolymer.[9] These polymer–monomer mixtures were then shaken at 50° and examined carefully and independently by a number of observers. A layer or droplets of residual monomers could be seen in the charges corresponding to 45 and 50% conversion, but not in those of 55 and 60% conversion. This is in agreement with the inference from the pressure measurements. It is of interest to note also, that there appeared to be a pronounced decrease in the viscosity of the latex upon the complete solution of the residual monomers. The charges corresponding to 45 and 50% conversion were noticeably more viscous than those of 55 and 60% conversion.

The agreement of observed and calculated values below 52% conversion shows that the assumption made in the calculation is essentially correct, which means that the monomers dissolve in the polymer particles in almost the same proportions that they are present in the total monomer mixture.

The conclusion that the composition of the monomer layer is not changed much by distribution with the polymer particles could be checked by direct experiments on non-polymerizing systems. (The measurements were not made with the accurate manometric method, but with the pressure gage-injection method.) To the stripped latex previously referred to, were added various amounts of different monomer mixtures, the amounts being chosen so that some undissolved monomer was present (*i. e.*, equivalent conversion less than 50%). It was found that the pressure of the monomer–polymer mixture was the same (within the limits of experimental uncertainty, 1–2%) as the pressure of the monomer mixture alone. This proves in a direct way, that there is little change in the composition of a butadiene–styrene mixture on dissolving in polymer.

Measurements of precision greater than 1% reveal a difference in the composition as a result of the distribution of the monomers between the phases. Consider the situation at exactly 40% conversion. The copolymer contains 18.7% styrene,[9] which corresponds to 70.8% butadiene in the total residual monomers. If the free monomer phase had this composition the hydrocarbon pressure would be 3527 mm. The actual pressure is 3576 mm. which corresponds to 72.5% butadiene in the monomer phase. Therefore the oil phase is slightly richer in butadiene than would correspond to the composition of the entire mixture, which means that relatively more styrene than butadiene is dissolved in the polymer particles.

If the solubility of butadiene in the copolymer were known, the amount of each monomer which is dissolved in the copolymer could be calculated since the compositions of the total monomer mixture and of the separate monomer phase are known. As an approximation, the solubility of butadiene in the copolymer may be taken equal to the solubility in polybutadiene, which is known from the observed pressure drop to be about 48/52 or 0.92 g. of monomer per g. of polymer. With this assumption, it may be calculated that at 40% conversion, 87% of the residual butadiene and 88% of the residual styrene are dissolved in the polymer, and at 20% conversion, about 32% of the residual butadiene and 37% of the residual styrene are dissolved. It should be emphasized that these calculated values are of only an approximate nature.

I wish to thank Dr. I. M. Kolthoff for many discussions and suggestions.

Summary

The pressure of the residual monomer(s) has been measured during the emulsion polymerization of butadiene and of butadiene–styrene mixtures. During the emulsion polymerization of butadiene the monomer pressure is constant and equal to that of pure butadiene as long as a separate phase of undissolved butadiene is present.

The first drop in pressure corresponds to the disappearance of the phase of residual monomer by solution in the polymer. This occurs at about 52% conversion corresponding to a "solubility" of 0.92 g. of butadiene per g. of polybutadiene. This solubility is approximately the same at 30 and at 50°, and is unaffected by a sixteen-fold variation in the amount of soap used in preparing the emulsion charges. Equilibrium as regards distribution of monomer between the oil phase and the polymer phase appears to be maintained during the polymerization at 50°.

During the emulsion copolymerization of butadiene–styrene, the pressure changes continuously from the start of the reaction because of the change in the composition of the copolymer which is formed. At about 50–52% conversion a fairly abrupt drop in pressure occurs corresponding to the solution of excess monomers. The composition of the oil phase corresponds closely to the composition of the total residual monomers, which indicates that only a small change in composition of a butadiene–styrene mixture results from its distribution between the polymer and the oil phase.

MINNEAPOLIS, MINNESOTA RECEIVED AUGUST 16, 1948

[CONTRIBUTION FROM HOWARD UNIVERSITY]

Absorption Spectra of Azines and Dianils[1]

BY LLOYD N. FERGUSON AND THOMAS C. GOODWIN[2]

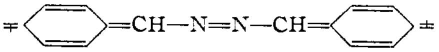
The order of increasing chromophoric power of the common chromophores was early recognized to be

$$C{=}C \quad C{=}N \quad C{=}O \quad N{=}N \quad C{=}S$$

This order has been attributed by several persons[3,4,5,6,6a] to the relative amounts of strain[7] within the double bonds. Other factors being equal, with increasing strain within the bond there results a less stable ground state, causing a smaller difference in the potential energies of the ground and first excited states and, hence, an absorption of light of longer wave length.

What appears to be at first glance an anomaly to this generalization is the fact that azines, which contain two stronger chromophores than a polyene hydrocarbon containing the same number of double bonds, absorb light of shorter wave length than the latter compounds. For instance, Lewis and Calvin[3] have pointed out that benzalazine, $C_6H_5CH{=}N{-}N{=}CHC_6H_5$, ($\lambda_{max.}$ = 301 mμ) absorbs light at shorter wave lengths than does 1,4-diphenylbutadiene, $C_6H_5CH{=}CH{-}CH{=}CHC_6H_5$ ($\lambda_{max.}$ = 334 mμ), and Blout and Fields[8] have reported that polyene azines of the generic formula $CH_3(CH{=}CH)_nCH{=}N{-}N{=}CH(CH{=}CH)_nCH_3$ have maximum absorption bands at shorter wave lengths than do the corresponding aliphatic polyene hydrocarbons with the same number of double bonds.

Lewis and Calvin have explained this on the basis of the "strain" theory by saying that due to the highly strained N=N bond in one of the predominant excited states of benzalazine



the potential energy of the excited state is raised. Although the ground state of the azine may lie above that of the diene, there is a larger difference between the energies of the first excited state and the ground state for the azine to the extent that it absorbs at shorter wave lengths. Blout and Fields have offered a different explanation. Their concept is to place greater emphasis on the contribution of forms Ib and Ic than on Ia to the resonance of the azines which, they believe, favors absorption at shorter wave lengths.[9]

$$CH_3{-}CH{=}CH{-}CH{=}N{-}N{=}CH{-}CH{=}CH{-}CH_3 \quad \text{I}$$

$$CH_3{-}\overset{\mp}{C}H{-}CH{=}CH{-}N{=}N{-}CH{=}CH{-}\overset{\pm}{C}H{-}CH_3 \quad \text{Ia}$$

$$CH_3{-}\overset{+}{C}H{-}CH{=}CH{-}\overset{-}{N}{-}N{=}CH{-}CH{=}CH{-}CH_3 \quad \text{Ib}$$

$$CH_3{-}CH{=}CH{-}CH{=}\overset{-}{N}{-}N{-}CH{=}\overset{+}{C}H{-}CH_3 \quad \text{Ic}$$

When the three compounds, glyoxaldianil ($C_6H_5N{=}CH{-}CH{=}NC_6H_5$), diphenylbutadiene and benzalazine are considered from Lewis' and Calvin's viewpoint, one may expect the dianil to absorb at longer wave lengths than the diene because, first, the dianil possesses two stronger chromophores and, second, the resonance of structures IIa, IIb and IIc for the dianil makes a greater contribution to the excited state than does the resonance of the corresponding ionic forms of the hydrocarbon.

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(1) Data presented before the Organic Division of the American Chemical Society, Sept., 1947.

(2) Present address: Duriron Co., Dayton, Ohio.

(3) G. N. Lewis and M. Calvin, *Chem. Reviews*, **25**, 273 (1939).

(4) S. Dutt, *J. Chem. Soc.*, 1171 (1926).

(5) A. A. Kharkharov, *Chem. Abstracts*, **34**, 4065 (1940).

(6) L. N. Ferguson, *Chem. Reviews*, in press.

(6a) S. H. Lee and F. A. Matsen, Paper number 33 presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society at Portland, Ore., September 14, 1948.

(7) The word "Strain" is used as a mechanical way of referring to the relative potential energy of a particular structure.

(8) E. R. Blout and M. Fields, THIS JOURNAL **70** 189 (1948).

(9) The author is of the opinion that due to the greater electronegativity of nitrogen over carbon, the forms Ib and Ic do make a contribution to the resonance of the azines but this only tends to lower the potential energy of the excited states and would lead to absorption at longer wave lengths than the azines might have **if** these ionic forms were not possible contributors. This contribution, however, is too small to outweigh the opposite effect caused by the strain in the N=N bond.