[CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORY OF POLAROID CORPORATION]

The Absorption Spectra of Certain Aldazines

BY ELKAN R. BLOUT AND RALPH M. GOFSTEIN

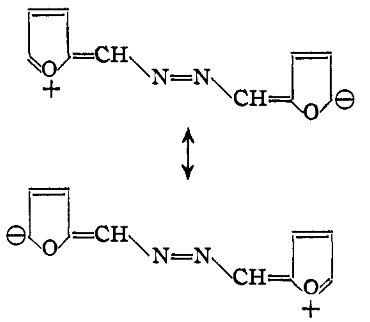
The ultraviolet spectra of the azines obtained from benzaldehyde, cinnamaldehyde and 5-phenylpentadienal have been recorded by previous workers,[1] who have noted the effect of the nitrogen atoms in removing the fine structures of the bands associated with the corresponding diphenylpolyenes. The absence of fine structure simplifies the study of the effect of substituent groups upon spectra.

In the present communication, the ultraviolet absorption spectra of substituted aldazines have been examined with a view toward extending our knowledge of the correlation of light absorption and structure. We are concerned with the spectra of compounds of the general type

$$R—(CH{=}CH)_x—CH{=}N—N{=}CH—(CH{=}CH)_x—R$$

where R represents an aromatic group, and x is either 0 or 1. Since many substituted aromatic aldehydes are available, aldazines of the above type may be prepared conveniently by reaction with hydrazine.

We have reëxamined the spectra of benzalazine and cinnamalazine (Fig. 1) and have found the maxima to be at 300 and 352 mμ in agreement with Radulescu and Alexa.[1,2] A comparison of the spectra of 1,1′-naphthalazine with benzalazine shows the expected displacement of the absorption bands toward longer wave lengths characteristic of a more extensively conjugated resonating system. The azine from furfuraldehyde shows an absorption maximum at 335 mμ, which is a displacement of 35 mμ as compared with benzalazine. This may be explained by the relatively large contribution of dipolar structures such as I and II.



I

II

The spectra of the isomeric nitrobenzalazines (Fig. 2) indicate the effect of positional substitution on light absorption. The *p*-substituted compound, having a maximum at 318 mμ, shows a

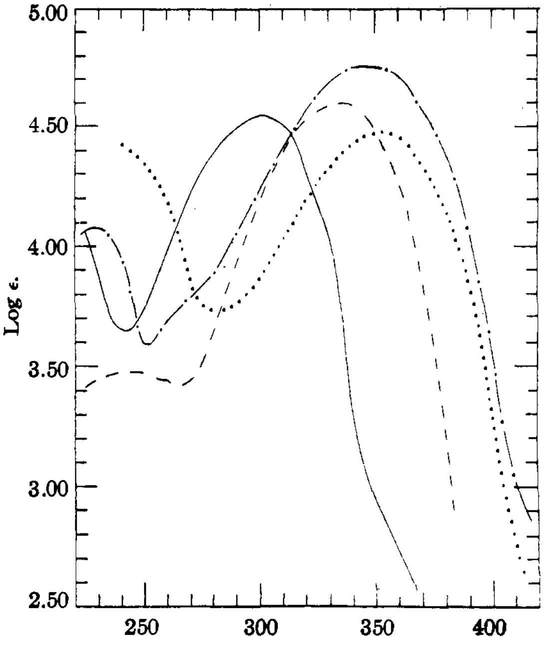


Fig. 1.— ————, benzalazine; —·—·—·—, cinnamalazine; - - - - - - - - -, furfuralazine; . . . ., 1,1′-naphthalazine.

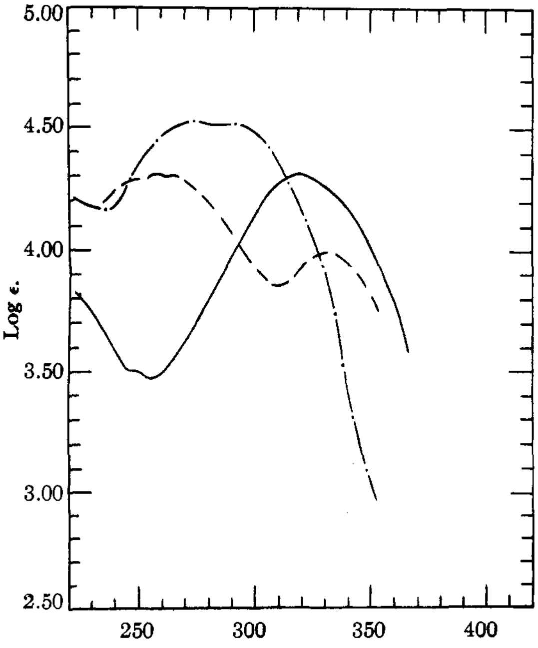


Fig. 2.— ————, 4,4′-dinitrobenzalazine; —·—·—·—, 3,3′-dinitrobenzalazine; - - - - - - - - -, 2,2′-dinitrobenzalazine.

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(1) Radulescu and Alexa, *Ber.*, **64**, 2230 (1931).

(2) The extinction coefficients, however, while appearing to differ in the two determinations, are actually similar, the difference being in the definition of ε.

bathochromic displacement compared to benzalazine. 3,3'-Dinitrobenzalazine shows no well-defined maximum but rather a rudimentary separation at the band head from 265 to 295 mμ. The *o*-nitro compound, 2,2'-dinitrobenzalazine, shows two distinct absorption bands; the shorter wave length band exhibits fine structure, whereas the band at longer wave length shows a single maximum at 332 mμ.

Analogous phenomena are observed with the isomeric hydroxybenzalazines (Fig. 3). The *p*-hydroxy compound has a single absorption band with a maximum at 335 mμ; whereas the *m*-hydroxyazine has a maximum at 300 mμ and an inflection point at 325 mμ. In the *o*-hydroxy compound, on the other hand, there is complete separation into two bands, the maxima lying at 295 mμ and 355 mμ, respectively.

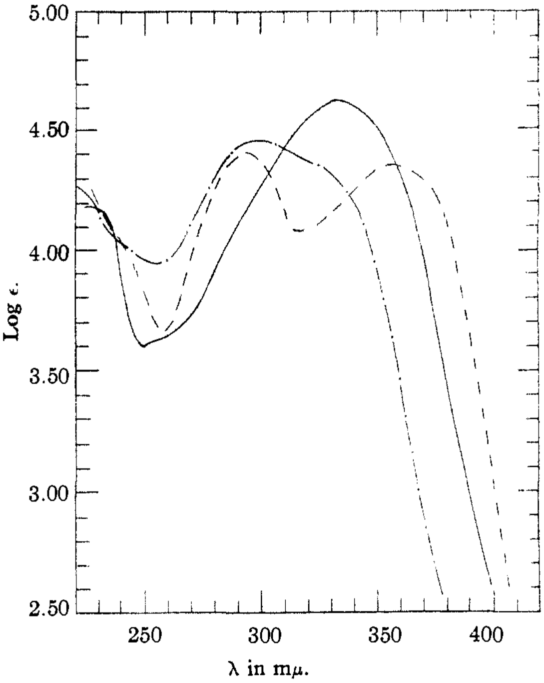


Fig. 3.——————, 4,4'-dihydroxybenzalazine; —·—·—, 3,3'-dihydroxybenzalazine; ----------, 2,2'-dihydroxybenzalazine.

This same effect is apparent upon consideration of the spectra of 4,4'-dihydroxy-1,1'-naphthalazine and 2,2'-dihydroxy-1,1'-naphthalazine (Fig. 4). The unsubstituted naphthalazine shows a single peak at 355 mμ, but in the 4-hydroxy compound the maximum is displaced to 385 mμ and shows no inflection points or band splitting. The displacement is of about the same magnitude observed with the corresponding benzal compounds (*cf.* Figs. 1 and 3). 2,2'-Dihydroxy-1,1'-naphthalazine, on the other hand, shows two absorption maxima, one at 330 mμ and the other at 409 mμ, the same region in which the corresponding 4-hydroxy compound shows only one.

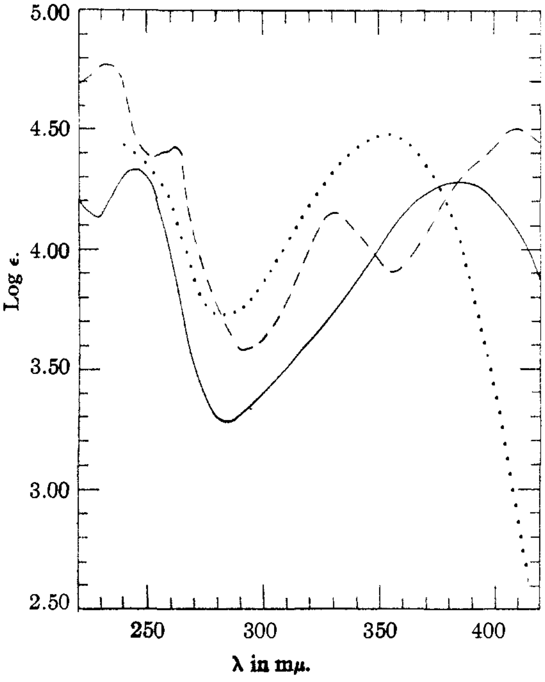
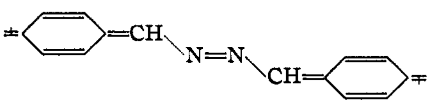


Fig. 4.—. . . . ., 1,1'-naphthalazine; ————, 4,4'-dihydroxy-1,1'-naphthalazine; ---------, 2,2'-dihydroxy-1,1'-naphthalazine.

The recent correlations[3,4] between resonance and color in organic substances afford an explanation of these results. Color may be attributed to transitions to excited states of high dipole moment. Therefore, any substituents affecting the polarizability (or the dipole moment of the excited states) will affect the light absorption. Furthermore, planar molecules may be considered to have two polarizabilities at right angles to each other, and compounds such as benzalazine may be treated as linear when one considers the limit structures of the excited state, III.

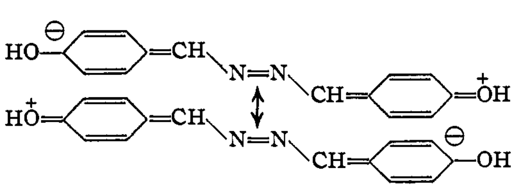


III

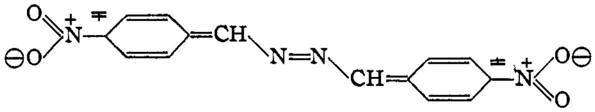
Likewise, the symmetrically *p*-substituted benzalazines may be considered as linear since the effect of the substituents will be directed along the same axis. Therefore, only positional differences in absorption spectra would be expected between unsubstituted benzalazine and the *p*-substituted benzalazines. This is, in fact, the case (*cf.* Figs. 1, 2, 3, 5). This line of reasoning may be extended to explain the differences in the position of the maxima of the *p*-substituted benzalazines. Assuming transitions to forms such as III are responsible for the absorption maximum at 300 mμ of benzalazine, then forms such as IV

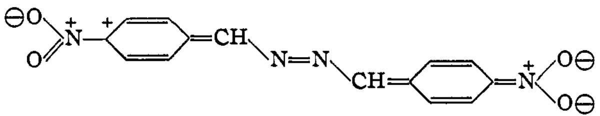
(3) Lewis and Calvin, *Chem. Rev.*, **25**, 273 (1939); Bury, This Journal, **57**, 2115 (1935); Pauling, *Proc. Natl. Acad. Sci.*, **25**, 577 (1939); Mulliken, *J. Chem. Phys.*, **7**, 121, 364, 570 (1939).

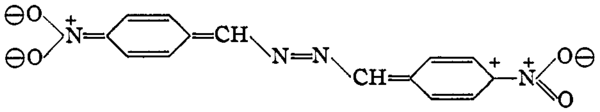
(4) *Cf.* Pauling in "Organic Chemistry," H. Gilman, Editor, 1943, 2nd ed., Vol. II, pp. 1944 ff.

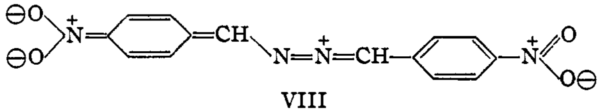

IV

must account for the maximum at 335 mμ of the *p*-hydroxy compound. In effect the hydroxyl groups increase the length of the absorbing system and thus shift the maximum to longer wave lengths.[5] In the corresponding *p*-nitro compound, the single absorption peak may be attributed to the preponderance of essentially linear forms such as V, VI, VII and VIII.[6]

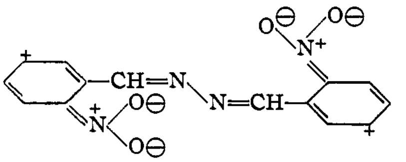

V


VI

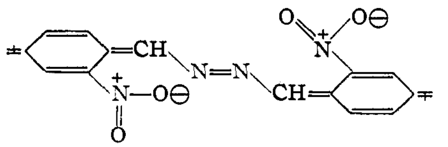

VII


VIII

In the *o*-substituted compounds, resonance structures are permitted which involve charge oscillation non-colinear with the main chromophoric axis and forms such as IX for *o*-nitrobenzalazine may contribute to an excited state.


IX

It is not impossible that the peak at 255 mμ[7] is due to transitions to excited states corresponding to forms such as IX, whereas the maximum at 325 mμ involves more nearly linear forms such as X in which the nitro groups add to the electron mobility of the system. *m*-Nitrobenzalazine exhibits incomplete band separation. The maximum at 295 mμ is again attributed to linear structures analogous to the unsubstituted compound (*cf.* III), whereas the lower wave length maximum probably involves forms similar to IX, as the band occurs in the same region as the maximum observed in nitrobenzene.[7]


X

Spectra of the same type as those of the nitro compounds are observed in the *o*- and *m*-hydroxybenzalazines, but the maxima lie at much longer wave lengths. For example, 2,2′-dihydroxybenzalazine has absorption bands at 295 mμ and 355 mμ. It is apparent that the shorter wave length band is due to resonance forms similar to those responsible for the absorption of benzalazine (III), while the longer wave length band may be attributed to non-colinear forms. The difference between the effect of the nitro and hydroxyl groups may be attributed to their electronic properties. The hydroxyl group tends to give up electrons to the aromatic ring, whereas the nitro group tends to draw electrons from the ring.[8] Substituents such as hydroxyl or methoxyl that tend to add electrons will have a bathochromic effect on benzalazine while groups that take out electrons will have a hypsochromic effect. It should be pointed out that double maxima have been noted in the spectra of *o*-nitroaniline, *o*-nitrophenol, *o*-nitrotoluene[9] and *o*-hydroxy- and *o*-methoxybenzaldehyde.[10]

The possibility of other explanations for the band splitting in the *o*-substituted compounds has been considered since it is evident that chelation may occur in the *o*-hydroxyazines. Other workers[9,11] have attributed double maxima observed in absorption spectra to inter- and intramolecular hydrogen bonding. That chelation of the *o*-hydroxyl group and the azine nitrogen in 2,2′-dihydroxybenzalazine is not the cause of the band splitting observed is shown by examination of the spectrum of the corresponding methyl ether,

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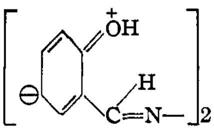
[5] *Cf.* Hausser, Kuhn and Seitz, *Z. physik. Chem.*, **B29**, 391 (1935).

[6] It is recognized that, since 4,4′-dinitrobenzalazine does not absorb at as high wave lengths as the corresponding hydroxy azine, the importance of forms that contribute to the lengthening of the conjugate absorption must be less, *e. g.*, forms VI and VII. The smaller contribution and instability of such forms are in turn probably due to the presence of adjacent positive charges.

[7] *Cf.* Absorption spectrum of nitrobenzene; maximum 255 mμ: Wolf and Herold, *Z. physik. Chem.*, **B13**, 201 (1931).

[8] It is interesting to note that one of the main resonance forms of 2,2′-dihydroxybenzalazine corresponds closely in electronic configuration to that of *o*-nitrophenol; that is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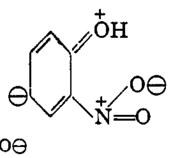
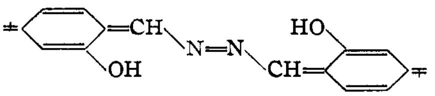


where the $\text{C}(\text{H})\!=\!\text{N}$ is replaced by the $\overset{+}{\text{N}}(\text{O}^{\ominus})\!=\!\text{O}$. *o*-Nitrophenol has an absorption maximum at 355 mμ[9] as does 2,2′-dihydroxybenzalazine. We attribute this maximum to transitions to forms such as that above which are obviously non-colinear with resonance forms such as



to which we attribute the maximum at 295 mμ.

[9] Dede and Rosenberg, *Ber.*, **67**, 147 (1934).

[10] Morton and Stubbs, *J. Chem. Soc.*, 1347 (1940).

[11] Shepherd and Newsome, THIS JOURNAL, **64**, 2937 (1942).

TABLE I

Compound	M. p., °C. reported	Observed m. p., °C. (cor.)	Crystn. solvent	$\lambda_{max.}$ in mμ	log ε
Benzalazine	93[a]	92.5–93	Pyridine	300	4.56
Cinnamalazine	162[a]	170–171	Ethanol	352	4.76
Furfuralazine	111–112[b]	110–111.5	Ethanol	335	4.60
1,1'-Naphthalazine	156[c]	156–157	Ethanol	354	4.48
4,4'-Dinitrobenzalazine	297[d]	297–298	Pyridine	318	4.53
3,3'-Dinitrobenzalazine	196–197[d]	196–197	Butanol	265–295	4.51–4.53
2,2'-Dinitrobenzalazine	205[d]	205–206	Dioxane	260	4.32
				332	3.98
4,4'-Dihydroxybenzalazine	c. 268[e]	270 (dec.)	Ethanol	335	4.63
3,3'-Dihydroxybenzalazine	204–205[f]	204–205	Ethanol	300	4.46
				~325	4.40
2,2'-Dihydroxybenzalazine	214[g]	213–214	Ethanol	295	4.40
				355	4.36
4,4'-Dihydroxy-1,1'-naphthalazine	236[h]	239–240 (dec.)	Dioxane	245	4.33
				385	4.29
2,2'-Dihydroxy-1,1'-naphthalazine	>290[i]	>300	Butanol	232	4.77
				267	4.43
				330	4.16
				409	4.51
2,2'-Dimethoxybenzalazine	143[e]	143–144	Ethanol	293	4.11
				340	4.29
4,4'-Dimethoxybenzalazine	168–177[d] *liquid crystalline*	170–185 *liquid crystalline*	Pyridine	330	4.56

~ indicates an inflection point.

[a] Curtius and Jay, *J. prakt. Chem.*, [2] **39**, 27 (1889). [b] Minunni, *Gazz. chim. ital.*, **29**, II, 467 (1899). [c] Curtius, *J. prakt. Chem.*, [2] **85**, 393 (1912). [d] Knopfer, *Monatsh.*, **30**, 29 (1909). [e] Vorländer, *Ber.*, **39**, 803 (1906). [f] Noelting, *Ann. chim. phys.*, [8] **19**, 497 (1910). [g] Borsche, *Ber.*, **34**, 4297 (1901). [h] Gattermann, *Ann.*, **357**, 313 (1907). [i] Gattermann and von Horlacher, *Ber.*, **32**, 284 (1899).

2,2'-dimethoxybenzalazine (Fig. 5), in which compound chelation does not exist. The two maxima, at 290 mμ and 340 mμ, are displaced slightly toward shorter wave lengths as compared with the *o*-hydroxyazine (Fig. 3). We have also determined the spectrum of 4,4'-dimethoxybenzalazine and observed that there is only a single peak (Fig. 5). This curve again closely resembles the corresponding hydroxy compound except for a displacement of the maximum about 5 mμ to shorter wave lengths, which indicates a smaller contribution of the methoxyl group to dipolar structures, and hence its absorption band lies farther out in the ultraviolet.[4]

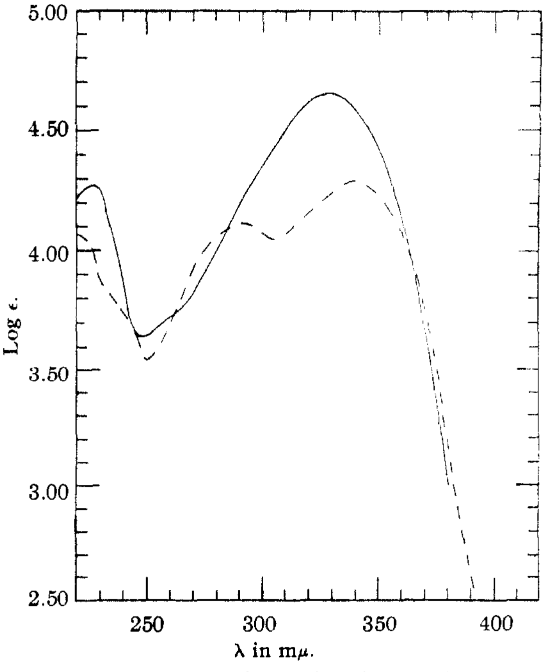


Fig. 5.— ———4,4'-dimethoxybenzalazine; - - - - - - - - - 2,2'-dimethoxybenzalazine.

Our viewpoint that the double peak observed in the azines substituted in the 2,2'-positions is not due to hydrogen bonding is further substantiated by the incipient band splitting shown in the spectra of the *m*-substituted benzalazines (Figs. 2 and 3). Intramolecular association in these compounds is impossible on steric grounds,[12] and, therefore, it may be assumed that the greater approach toward linearity of the *m*-substituted azines as compared with the *o*- accounts for the incomplete separation of the absorption bands in the former compounds.

The possibility that the single peaks observed in the unsubstituted and *p*-substituted azines are in reality composed of two bands at the same wave length has been considered. That this is probably not the case is evident from a consideration of the spectra of 2,2'-dihydroxy-1,1'-naphthalazine and 4,4'-dihydroxy-1,1'-naphthalazine (Fig. 4). It is found that one of the maxima of

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(12) *Cf.* Pauling, "Nature of the Chemical Bond," Chap. IX, Cornell Univ. Press, Ithaca, N. Y., 2nd edition, 1942.

the 2-hydroxylated compound has a higher extinction coefficient (log ϵ_1 4.51) than the single peak of the 4-hydroxylated compound (log ϵ, 4.29), which in turn is lower than the corresponding naphthalazine containing no hydroxyl groups (log ϵ, 4.48). If the curves that show only a single maximum were composed of two bands lying at the same place, it would be expected that the single peak would have a higher extinction coefficient than those of the peaks found in double peaked curves. Since one of the peaks of the doubly peaked curve is higher, we may assume that we are dealing with single absorption bands in the unsubstituted and *p*-substituted benzalazines.[13]

Acknowledgment.—The authors wish to express their appreciation to Dr. R. B. Woodward for many helpful discussions and to Mrs. D. C. Silverman, Mr. A. S. Makas, and Mr. E. Farmer for their valuable assistance in the determination of most of the absorption spectra recorded herein.

Experimental

The azines were prepared by shaking 2.3 moles of the corresponding aldehyde with 1 mole of 85% hydrazine hydrate in water or dilute ethyl alcohol. In some cases the hydrazone rather than the azine separated, but on addition of a drop of dilute hydrochloric acid to the solvent used in the recrystallization, the hydrazone was decomposed to the azine.

The absorption spectra measurements were made on a Beckmann quartz spectrophotometer model DU using a 1-cm. quartz cell and a hydrogen discharge tube as an ultraviolet source. Absolute ethyl alcohol was used as a solvent throughout.

Summary

The ultraviolet absorption spectra of several substituted aromatic aldazines have been determined. The band splitting noted in 2,2′-substituted benzal- and naphthalazines has been attributed to new absorption bands arising from the non-linearity of such molecules as compared with the unsubstituted and *p*-substituted azines.

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(13) We have not neglected to consider that the shorter wave length band in the spectra showing two maxima might be a second order band. 4,4′-Dihydroxybenzalazine is more closely a linear harmonic oscillator than the isomeric 3-hydroxy or 2-hydroxy compound on purely geometric grounds. Thus, assuming that the single absorption band of the 4-hydroxy compound is due to a transition $v = 0 \rightarrow v = 1$ (*i. e.*, a transition from the ground state to the first excited state) it is possible that the double maximum observed in the *o* isomer is actually the result of two transitions, $v = 0 \rightarrow v = 1$ and $v = 0 \rightarrow v = 2$ which are due to oscillations along the same direction in the molecule. The probability of a second order transition occurring in the *p*-hydroxy compound is zero; Lewis and Bigeleisen, THIS JOURNAL, **65**, 2107 (1943). The *o*-isomer has more or less anharmonicity due perhaps to resonance contributions involving charge oscillation non-colinear with the main chromophoric axis. This anharmonicity would make the probability of the transition $v = 0 \rightarrow v = 2$ relatively greater since the electronic levels would lie lower and closer together. An analogous argument would hold for the *m*-compounds with consideration of the fact that the mesomeric effect of the azimethylene chain would not give rise to so great an interaction as that expected for the *o*- and *p*-compounds so that the splitting would be less pronounced. Also the *m*-compound would presumably be a more nearly linear harmonic oscillator than the *o*-compound. But the extinction coefficients for the two bands are nearly equal, and the ratio of their frequencies is << 2, so that it seems unlikely that the shorter wave length maximum is a second order band.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

The Effects of Temperature on the Polymerization of Styrene

BY SAUL G. COHEN[1]

It now seems probable that the polymerization of vinyl compounds is a chain process involving at least the following types of reactions.[2a,b,c] Active centers are formed, either catalytically (B. p.) or by thermal activation (equations 1a and 1b). In peroxide catalyzed and thermal reactions, these active centers are free radicals. Polymer chains are formed by the successive additions of monomer (M) molecules to the radicals (equation 2). The radicals are capable of undergoing so-called chain transfer reactions in which a growing polymer chain ceases to grow, (P_n), transferring its active center to a monomer or solvent molecule, initiating the growth of a new chain (equation 3). The radicals seem to be destroyed in pairs, either by combination or by disproportionation (equation 4).

$$\text{B. p.} \longrightarrow R^* \tag{1a}$$

$$M + M \longrightarrow 2R^* \tag{1b}$$

$$R_n^* + M \longrightarrow R_{n+1}^* \tag{2}$$

$$R_n^* + M \longrightarrow P_n + R^* \tag{3}$$

$$R_n^* + R_m^* \longrightarrow P_{n+m} \text{ or } P_n + P_m \tag{4}$$

With a change in temperature of reaction, the rates of all these processes change, and it is not clear which of these steps is most important in leading to the observed effects of temperature change on polymerization reactions. As the temperature is raised in thermal polymerizations, the rate increases and the molecular weight or degree of polymerization (D. P.) of the product decreases, log D. P. being linear with $1/T$.[2b] This decrease in molecular weight may be explained by two mechanisms.

In one, based on the results of catalyzed polymerizations,[3a,b,c] it may be postulated that D. P. depends solely on the ratio of the rates of steps

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[1] National Research Fellow, University of California at Los Angeles, 1943–1944. Present address, Research Laboratory, Pittsburgh Plate Glass Company, Barberton, Ohio.

(2a) Price and Kell, THIS JOURNAL, **63**, 2798 (1941). (2b) Flory, *ibid.*, **59**, 241 (1937). (2c) Mayo, *ibid.*, **65**, 2328 (1943).

(3a) Schulz and Husemann, *Z. physik Chem.*, **B34**, 187 (1936). (b) **B36**, 184 (1937); (c) **B39**, 246 (1938).