THE EFFECT OF SODIUM SULFITE ON THE ULTRAVIOLET ABSORPTION SPECTRA OF VARIOUS BENZENE DERIVATIVES

By

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A THESIS

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ACKNOWLEDGMENT

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INTRODUCTION

In the course of a spectrophotometric investigation of the exhaustion of various photographic developing agents, it was observed that a bathochromic shift in the ultraviolet absorption spectrum of hydroquinone occurred upon addition of sodium sulfite. Shifts in ultraviolet absorption spectra, especially those not involving the addition of auxochromes to the resonating system or chemical combination between the solvent and the compound, have received increasing attention in recent years.

Stenstrom and Reinhard[1] found that benzene derivatives with a ring hydroxyl group, such as phenol, tyrosine or resorcinol, gave a shift to longer wave lengths upon addition of alkali. The band characteristic of the molecule shifted towards longer wave lengths and increased in intensity when a certain alkalinity had been reached. These investigators attributed the shift to the change from the spectrum characteristic of the molecule to the spectrum characteristic of the compound ionized at the ring hydroxyl group.

In agreement with the effect of alkali on phenol, Morton and Stubbs[2] found that the absorption spectra of hydroxyaldehydes, hydroxyketones, and their methyl ethers, when studied in alkaline solution, show a bathochromic

displacement of the long wave band. Since a change in the initial energy state is indicated by this action, they observe that it must be the result of the induction effect of the substituents on the ring.

More recently, in 1947, Lemon[3] studied the effect of alkali on the ultraviolet absorption spectra of hydroxyaldehydes, hydroxyketones, and similar phenolic compounds. He found that the absorption bands of all these compounds were shifted towards longer wave lengths and, with the exception of m-hydroxybenzaldehyde, the intensity of light absorption was increased. Although all the ortho, meta, and para hydroxyaldehydes and hydroxyketones show spectral displacements in alkaline solution, it was the p-hydroxyaldehydes and the p-hydroxyketones that show the greatest wave length displacement of the long wave length bands and the greatest increase in absorption intensities.

Doub and Vandenbelt[4] studied the ultraviolet absorption spectra of mono- and para- disubstituted benzene derivatives. From these studies they formulated a general rule applying to such compounds: "Where ionization of a group attached to a benzene ring enhances the already existing tendency for electron transfer to or from the ring, the maximum of the primary band is shifted to longer wave length; where ionization diminishes this tendency, a shift

to shorter wave length results."

However, environmental conditions may produce spectral changes without involving changes in molecular structure, such as the ionization mentioned above. Klotz[5] investigated the effects of salts on the absorption spectra of various dyes and indicators. He found that although the effect of salts can be attributed largely to electrostatic interactions of the Debye-Huckel type, many specific interactions are found. These interactions are of the ion-dipole attraction type of the electrolyte with the solvent molecules.

Further effects of electrolytes in aqueous solution were studied by Merrill, Spencer, and Getty[6] and Merrill and Spencer[7]. In their investigation of the effect of sodium silicate on the absorption spectra of various dyes, they found spectral changes not due to the alkalinity of the silicate but attributable to sorption and electrostatic interaction of the dye ion with the sodium silicate ions.

It is the purpose of this investigation to study the bathochromic shift of the absorption spectra of hydroquinone and related compounds upon the addition of sodium sulfite and to characterize the sulfite effect.

EXPERIMENTAL PROCEDURE

Absorption measurements were made with a Beckman Quartz Spectrophotometer, Model DU[8]. The absorption cells were made of silica, the thickness of each being 1.000 ± 0.001 centimeter. The extinction readings were taken at intervals of 5 millimicrons, except in a few cases in the vicinity of absorption spectra maxima where the interval was 2 millimicrons.

The solvent in all cases was water. Laboratory distilled water was redistilled from all glass apparatus. The water was used as soon as possible to prepare the solutions to be run. A spectroscopic determination of the purity of the solvent indicated the absence of inorganic impurities.

The organic chemicals were of C.P. grade or better, most of them being Eastman Kodak white label grade. Durohydroquinone and diaminodurene dihydrochloride were obtained from Dr. A. Weissberger of the Synthetic Organic Research Laboratory of the Eastman Kodak Company. Cumohydroquinone and p-xylohydroquinone were obtained from a private source at the same company. The inorganic chemicals were also of C.P. quality or better, being in most cases either Baker's Analyzed or Eimer & Amend tested purity reagents.

The chemical or chemicals were accurately weighed out, placed in a thoroughly cleaned and dried volumetric flask, and then dissolved in the solvent. An alternate procedure was to make up separate organic and inorganic solutions of such concentration that when combined the resulting solution is of the desired concentration. The flask was then inverted and shaken vigorously, this procedure being repeated fifty times to insure complete dissolution of the solid material or mixing of the solutions. The repeated shaking is absolutely necessary in the case of the polysubstituted hydroquinones and the polysubstituted p-phenylenediamines to insure solution. After the shaking the absorption spectrum was then determined on the spectrophotometer.

TABLE I

Fig.	Organic Compound	Conc.	Sodium Sulfite Concentration	Maximum Organic	Maximum Org. & Sulfite	Shift
		(g./ml.)	(g./ml.)	(m mu)	(m mu)	(m mu)
1	Hydroquinone	0.000045	0.000090	288	305	17
2	Pyrocatechol	0.000045	0.000090	275	275	0
3	Resorcinol	0.000045	0.000090	275	275	0
4	p-Aminophenol hydrochloride	0.000045	0.000090	270	295	25
5	o-Aminophenol	0.000045	0.000090	285	285	0
6	m-Aminophenol	0.000045	0.000090	280	280	0
7	p-Phenylenediamine dihydrochloride	0.000045	0.000090	285	305	20
8	o-Phenylenediamine	0.000045	0.000090	290	290	0
9	m-Phenylenediamine	0.000045	0.000090	285	285	0
10	Elon (Monomethyl-p-aminophenol sulfate)	0.000045	0.000090	270	300	30
11	Amidol (Diaminophenol dihydrochloride)	0.000045	0.000090	285	310	25

TABLE I (continued)

Fig.	Organic Compound	Conc.	Sodium Sulfite Concentration	Maximum Organic	Maximum Org. & Sulfite	Shift
		(g./ml.)	(g./ml.)	(m mu)	(m mu)	(m mu)
12	Glycin (p-Hydroxy-phenyl glycin)	0.000046	0.000090	270	300	30
13	Phenol	0.000045	0.000090	270	270	0
14	Quinone	0.000045	0.000090	295	310	15
15	p-Cresol	0.000045	0.000090	275	275	0
16	Diacetylhydro-quinone	0.000045	0.000090	260	260	0
17	p-Methoxyphenol	0.000045	0.000090	288	288	0
18	Sulfanilamide	0.000009	0.000090	260	260	0
19	Diaminodurene dihydrochloride	0.000045	0.000090	270	270 295	0 25
20	Tetrachloro-hydroquinone	0.000045	0.000090	305	328	23
21	Durohydroquinone	0.000020	0.000090	272	263	9
22	Cumohydroquinone	0.000020	0.000090	260	262	2
23	p-Xylohydroquinone	0.000045	0.000090	288	252	36

TABLE I (continued)

Fig.	Compound	Conc.	Inorganic Conc.	Maximum Compound	Maximum Comp. & Inorg.	Shift
		(g./ml.)	(g./ml.)	(m mu)	(m mu)	(m mu)
24	Phloroglucinol	0.000045	0.000090 (Sodium Sulfite)	265	275	10
25	Hydroquinone Sodium Bisulfite	0.000045 0.000090	0.0001 (Sodium Carbonate)	288	308	20
26	Hydroquinone	0.000045	0.000090 (Potassium Sulfite)	288	300	12
27	Hydroquinone Cysteine mono-hydrochloride	0.000045 0.000090	0.0002 (Sodium Carbonate)	288	290	2
28	Hydroquinone	0.000045	0.0000225	288	295	7
			0.000045	288	300	12
			0.000090	288	305	17
			0.000180 (Sodium Sulfite)	288	300	12
29	Tetramethyl-p-phenylenediamine dihydrochloride	0.000045	0.000090	250	250 & 300	
		0.000180	0.000360 (Sodium Sulfite)	285	300	15

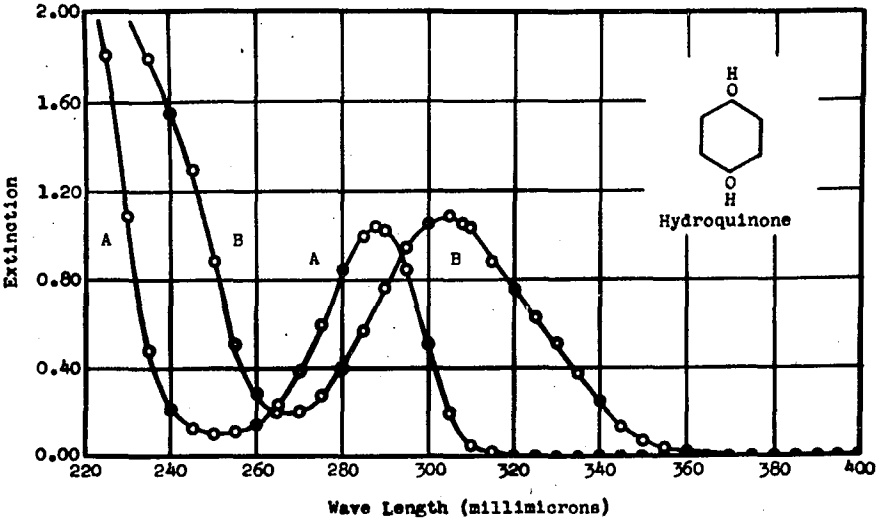

Figure 1. A-Hydroquinone (0.000045 g./ml.)
B-Hydroquinone (0.000045 g./ml.)
Sodium Sulfite (0.000090 g./ml.)

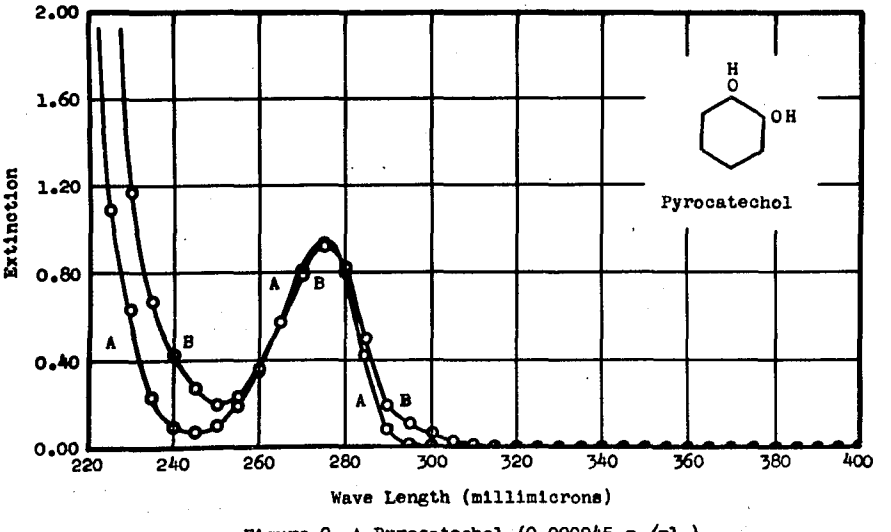

Figure 2. A-Pyrocatechol (0.000045 g./ml.)
B-Pyrocatechol (0.000045 g./ml.)
Sodium Sulfite (0.000090 g./ml.)

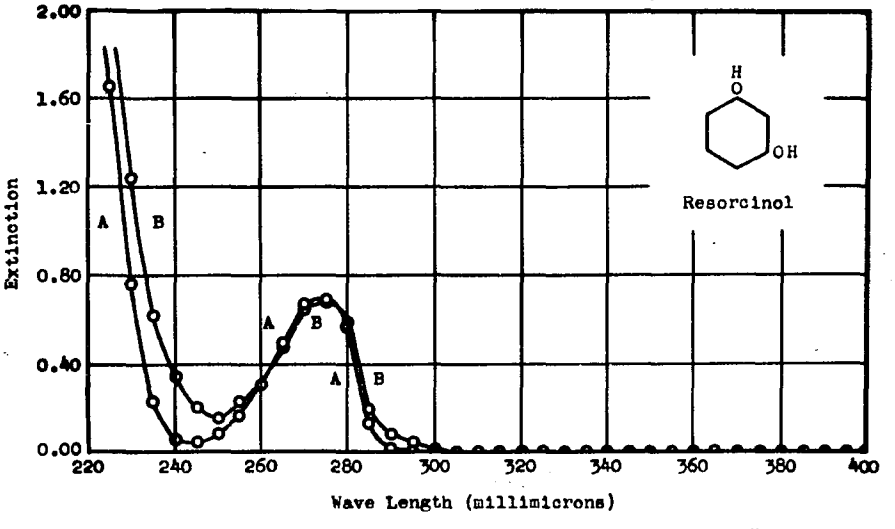

Figure 3. A-Resorcinol (0.000045 g./ml.)
B-Resorcinol (0.000045 g./ml.)
Sodium Sulfite (0.000090 g./ml.)

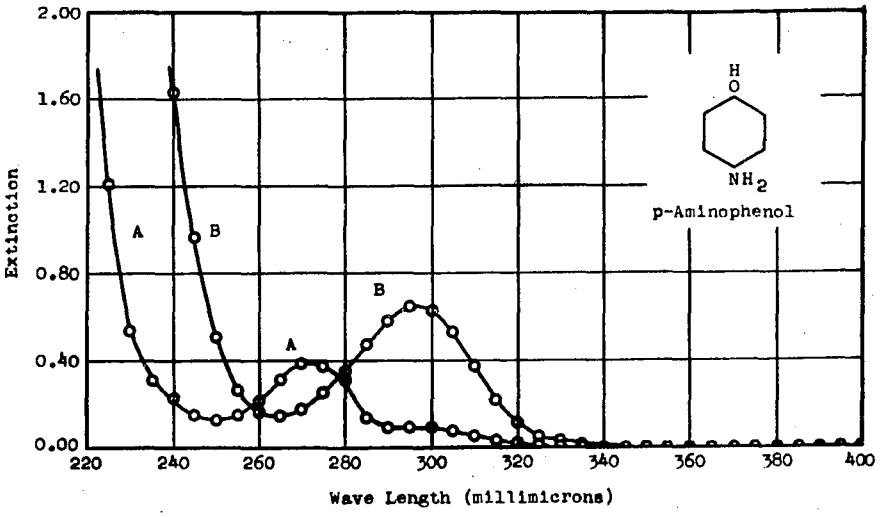

Figure 4. A. p-Aminophenol Hydrochloride (0.000045 g./ml.)
B. p-Aminophenol Hydrochloride (0.000045 g./ml.)
Sodium Sulfite (0.000090 g./ml.)

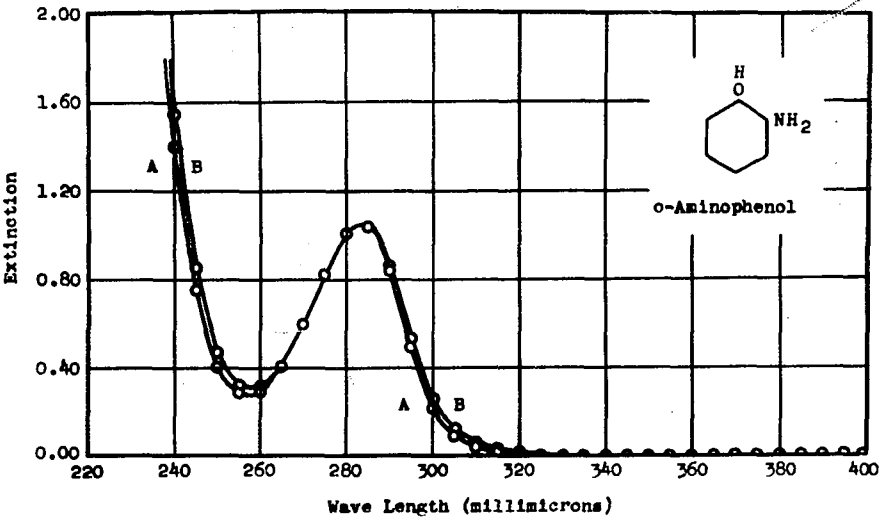

Figure 5. A. o-Aminophenol (0.000045 g./ml.)
B. o-Aminophenol (0.000045 g./ml.)
Sodium Sulfite (0.000090 g./ml.)

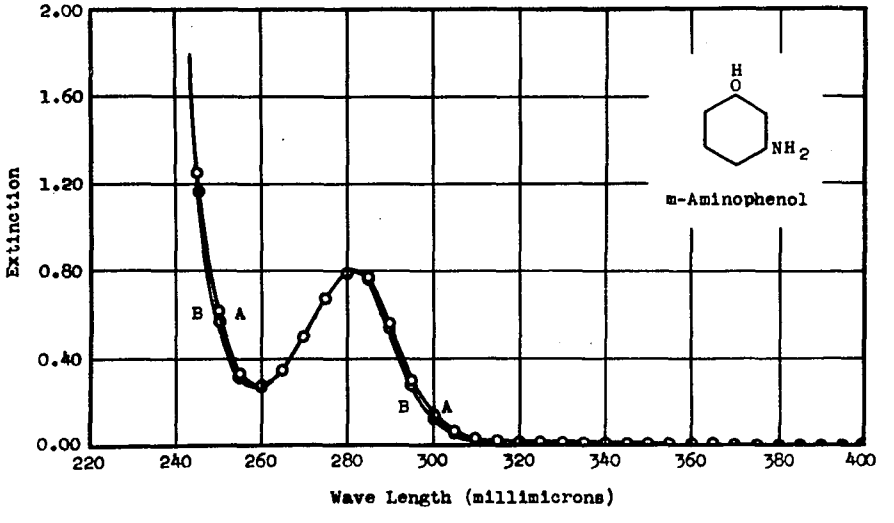

Figure 6. A. m-Aminophenol (0.000045 g./ml.)
B. m-Aminophenol (0.000045 g./ml.)
Sodium Sulfite (0.000090 g./ml.)

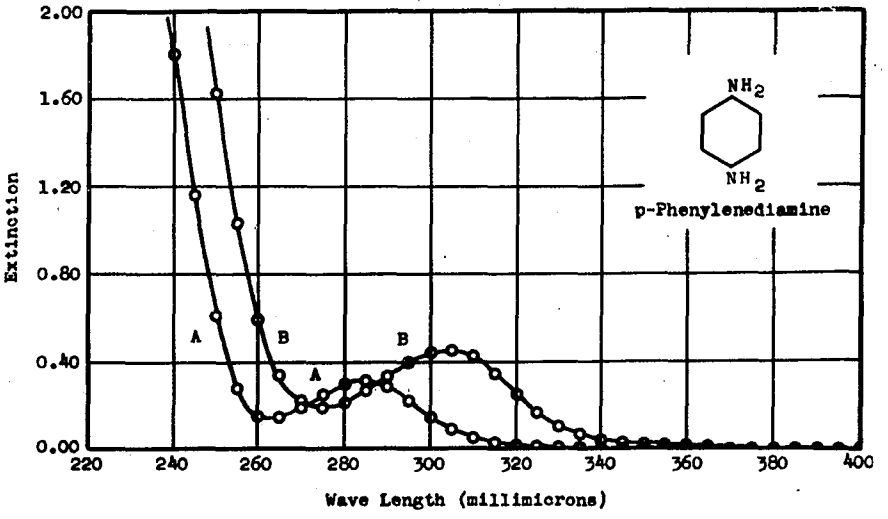

Figure 7. A. p-Phenylenediamine Dihydrochloride (0.000045 g./ml.)
B. p-Phenylenediamine Dihydrochloride (0.000045 g./ml.)
Sodium Sulfite (0.000090 g./ml.)

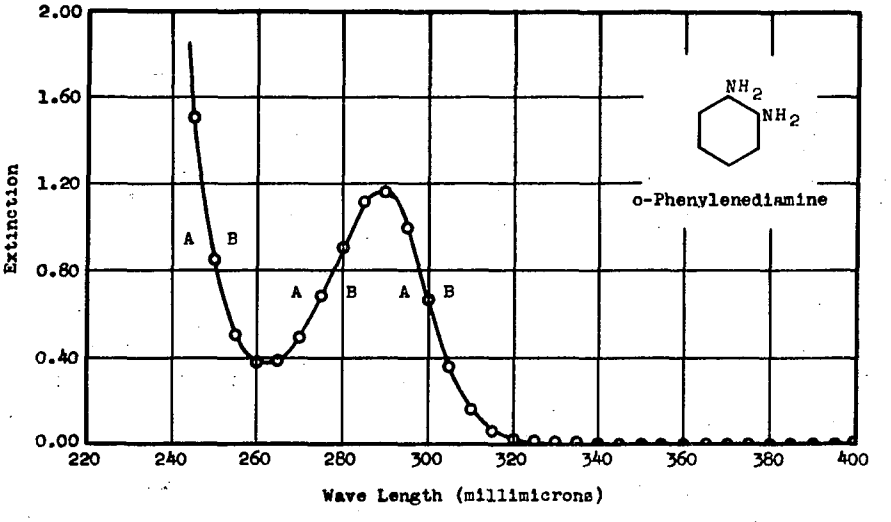

Figure 8. A. o-Phenylenediamine (0.000045 g./ml.)
B. o-Phenylenediamine (0.000045 g./ml.)
Sodium Sulfite (0.000090 g./ml.)

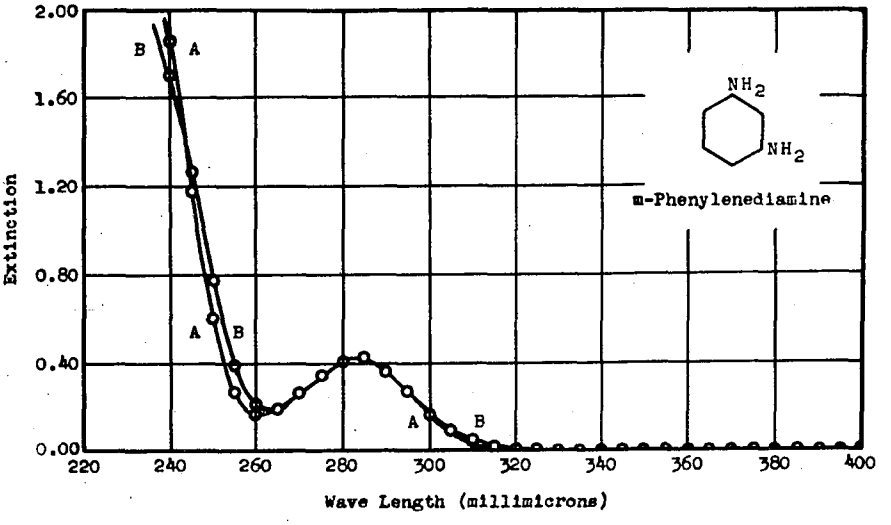

Figure 9. A. m-Phenylenediamine (0.000045 g./ml.)
B. m-Phenylenediamine (0.000045 g./ml.)
Sodium Sulfite (0.000090 g./ml.)

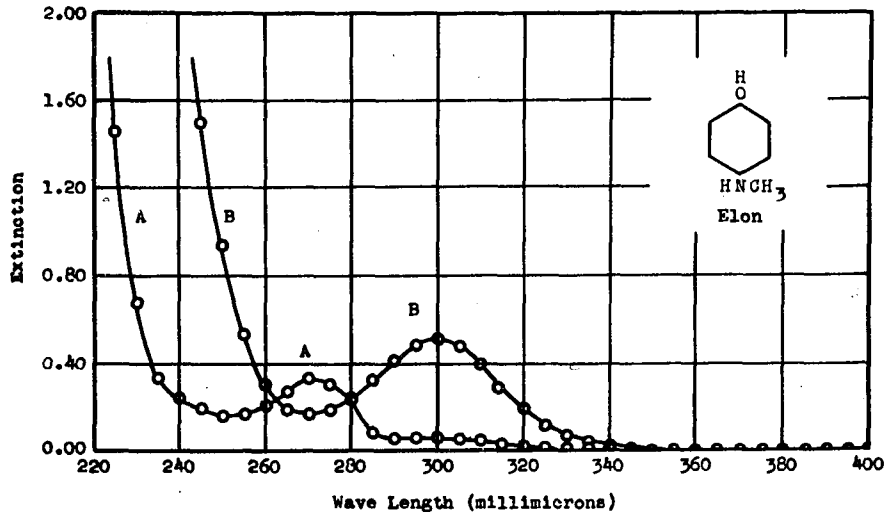

Figure 10. A. Elon (Monomethyl p-Aminophenol Sulfate) (0.000045 g./ml.)
B. Elon (Monomethyl p-Aminophenol Sulfate) (0.000045 g./ml.)
Sodium Sulfite (0.000090 g./ml.)

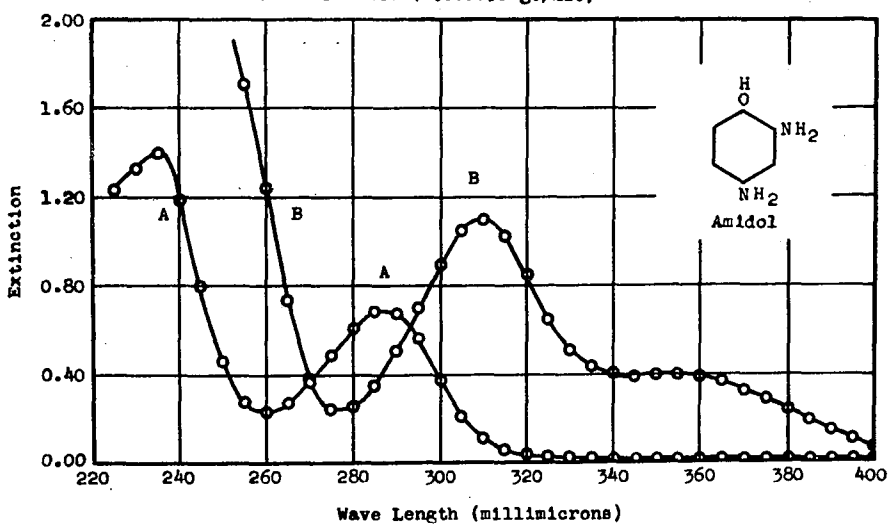

Figure 11. A. Amidol (Diaminophenol Dihydrochloride) (0.000045 g./ml.)
B. Amidol (Diaminophenol Dihydrochloride) (0.000045 g./ml.)
Sodium Sulfite (0.000090 g./ml.)

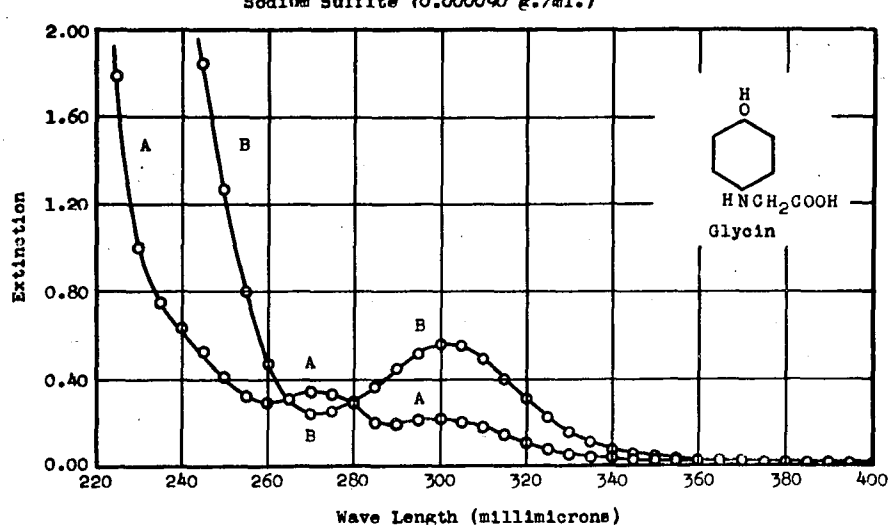

Figure 12. A. Glycin (p-Hydroxyphenyl Glycin) (0.000046 g./ml)
B. Glycin (p-Hydroxyphenyl Glycin) (0.000046 g./ml.)
Sodium Sulfite (0.000090 g./ml.)

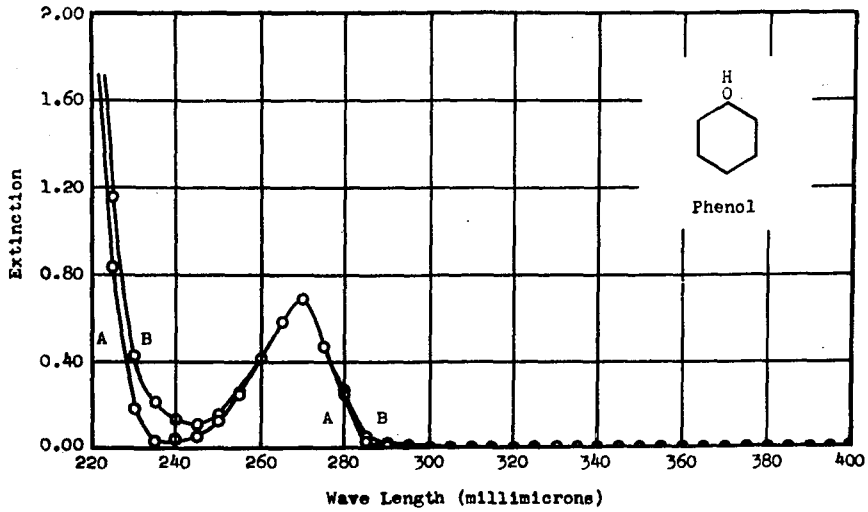

Figure 13. A. Phenol (0.000045 g./ml.)
B. Phenol (0.000045 g./ml.)
Sodium Sulfite (0.000090 g./ml.)

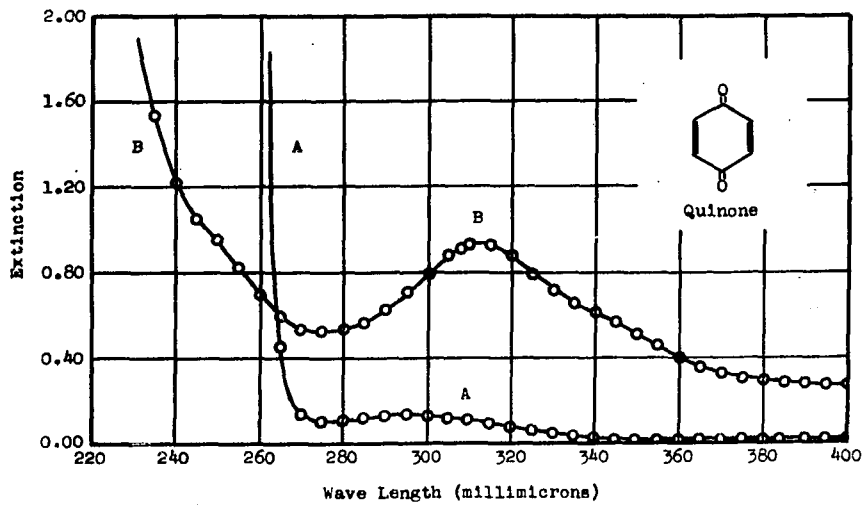

Figure 14. A. Quinone (0.000045 g./ml.)
B. Quinone (0.000045 g./ml.)
Sodium Sulfite (0.000090 g./ml.)

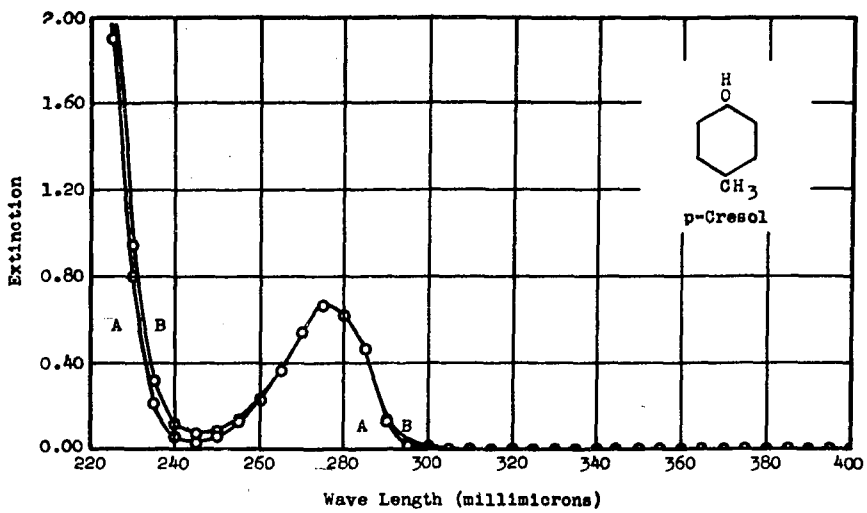

Figure 15. A. p-Cresol (0.000045 g./ml.)
B. p-Cresol (0.000045 g./ml.)
Sodium Sulfite (0.000090 g./ml.)

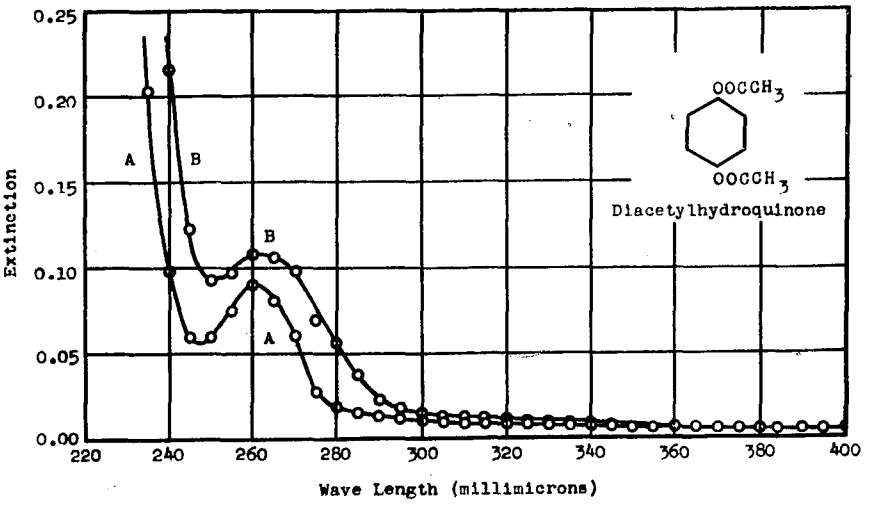

Figure 16. A. Diacetylhydroquinone (0.000045 g./ml.)
B. Diacetylhydroquinone (0.000045 g./ml.)
Sodium Sulfite (0.000090 g./ml.)

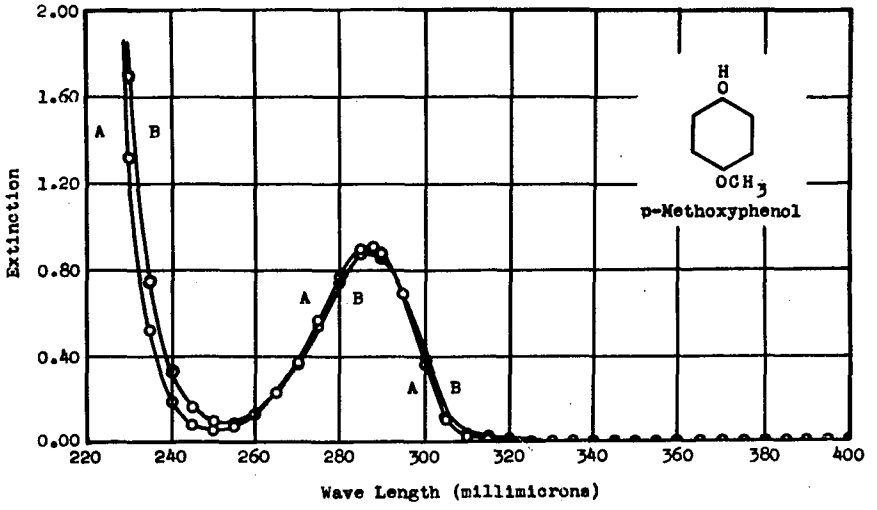

Figure 17. A. p-Methoxyphenol (0.000045 g./ml.)
B. p-Methoxyphenol (0.000045 g./ml.)
Sodium Sulfite (0.000090 g./ml.)

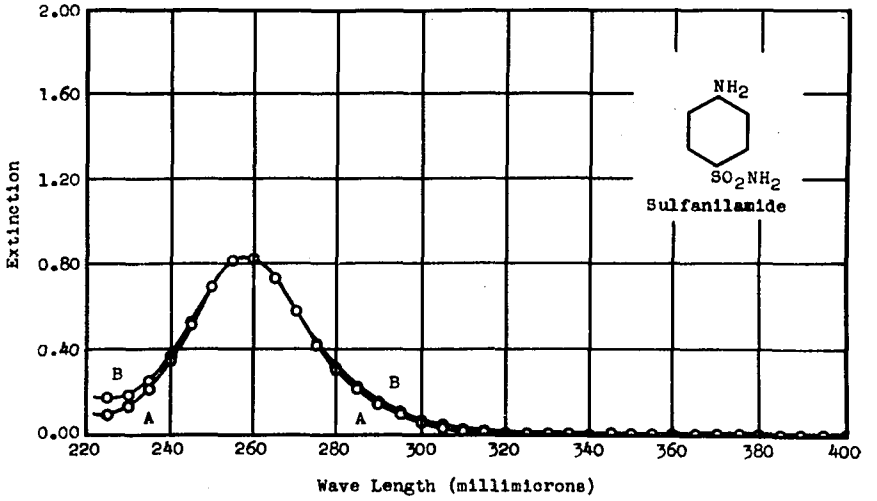

Figure 18. A. Sulfanilamide (0.000009 g./ml.)
B. Sulfanilamide (0.000009 g./ml.)
Sodium Sulfite (0.000090 g./ml.)

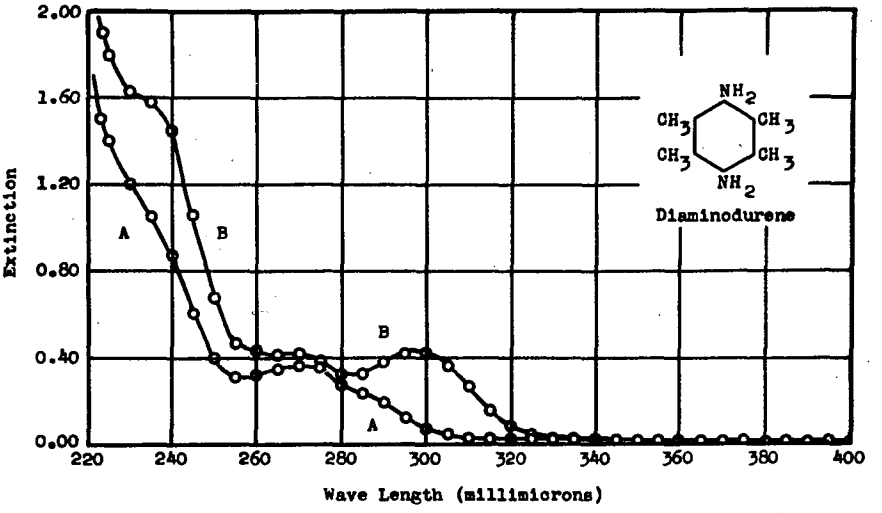

Figure 19. A. Diaminodurene Dihydrochloride (0.000045 g./ml.)
B. Diaminodurene Dihydrochloride (0.000045 g./ml.)
Sodium Sulfite (0.000090 g./ml.)

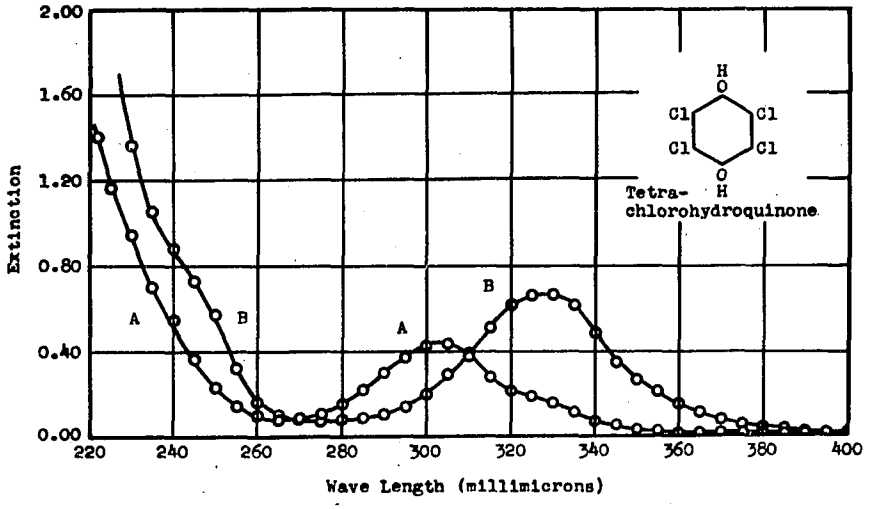

Figure 20. A. Tetrachlorohydroquinone (0.000045 g./ml.)
B. Tetrachlorohydroquinone (0.000045 g./ml.)
Sodium Sulfite (0.000090 g./ml.)

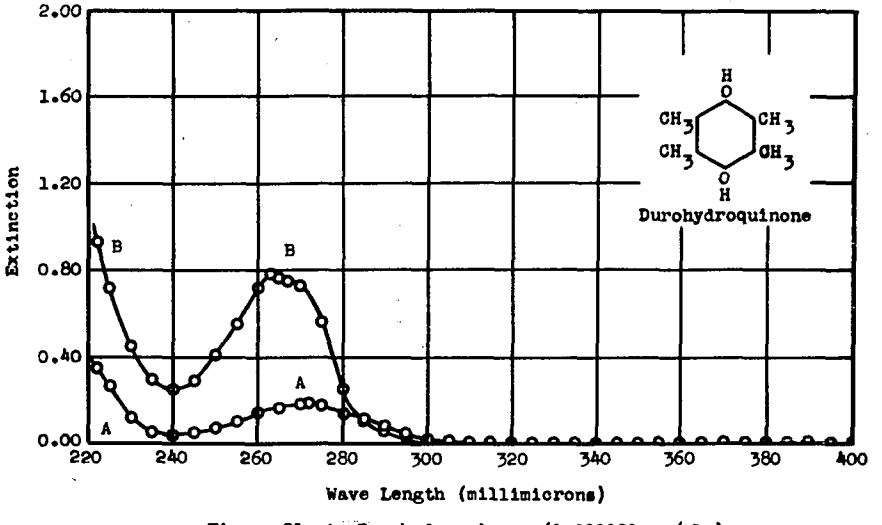

Figure 21. A. Durohydroquinone (0.000020 g./ml.)
B. Durohydroquinone (0.000020 g./ml.)
Sodium Sulfite (0.000090 g./ml.)

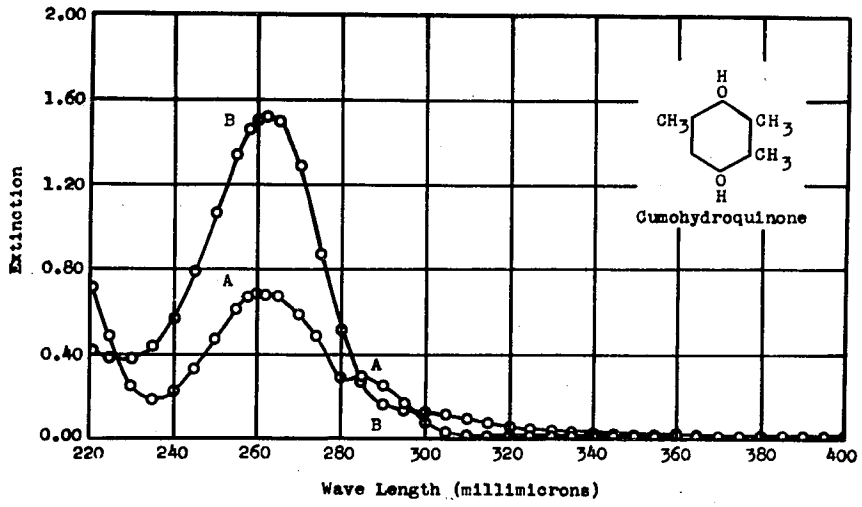

Figure 22. A. Cumohydroquinone (0.000020 g./ml.)
B. Cumohydroquinone (0.000020 g./ml.)
Sodium Sulfite (0.000090 g./ml.)

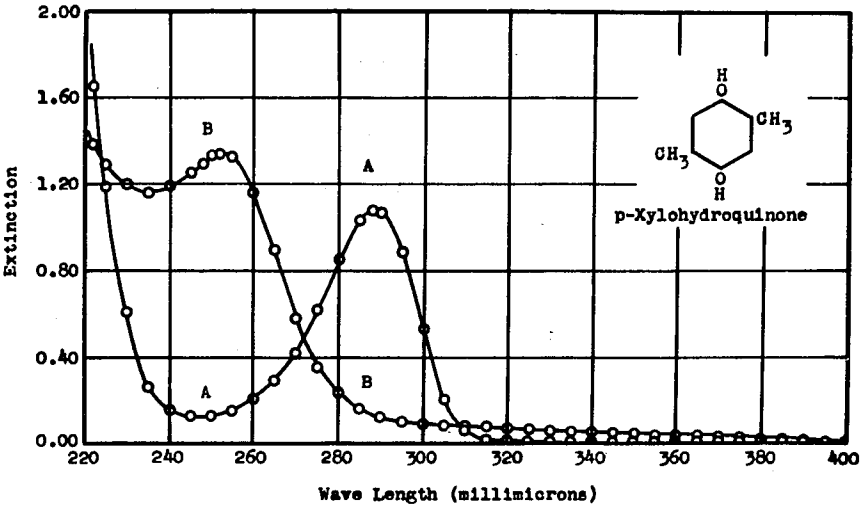

Figure 23. A. p-Xylohydroquinone (0.000045 g./ml.)
B. p-Xylohydroquinone (0.000045 g./ml.)
Sodium Sulfite (0.000090 g./ml.)

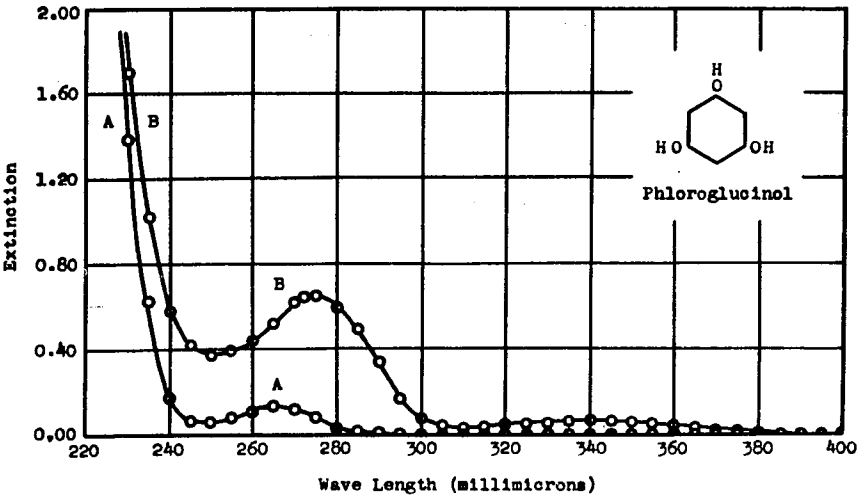

Figure 24. A. Phloroglucinol (0.000045 g./ml.)
B. Phloroglucinol (0.000045 g./ml.)
Sodium Sulfite (0.000090 g./ml.)

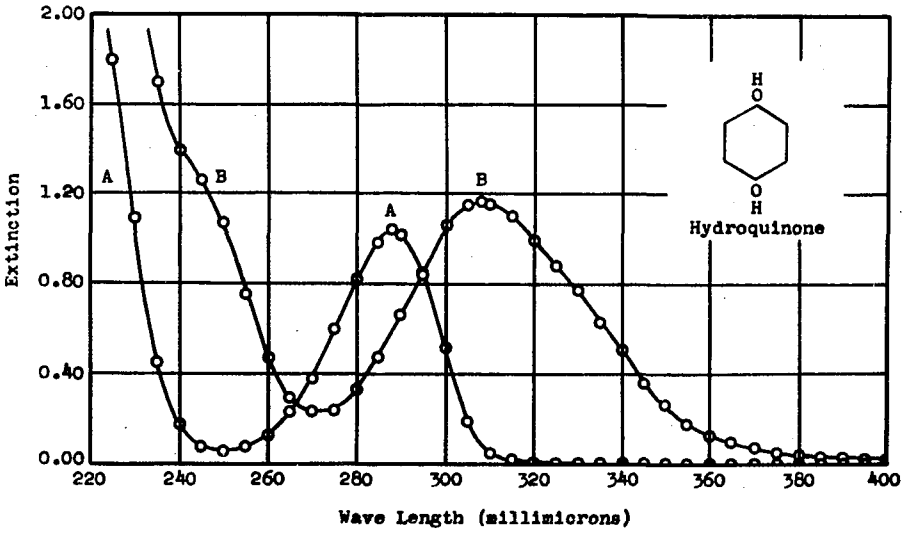

Figure 25. A. Hydroquinone (0.000045 g./ml.)
Sodium Bisulfite (0.000090 g./ml.)
B. Hydroquinone (0.000045 g./ml.)
Sodium Bisulfite (0.000090 g./ml.)
Sodium Carbonate (0.0001 g./ml.)

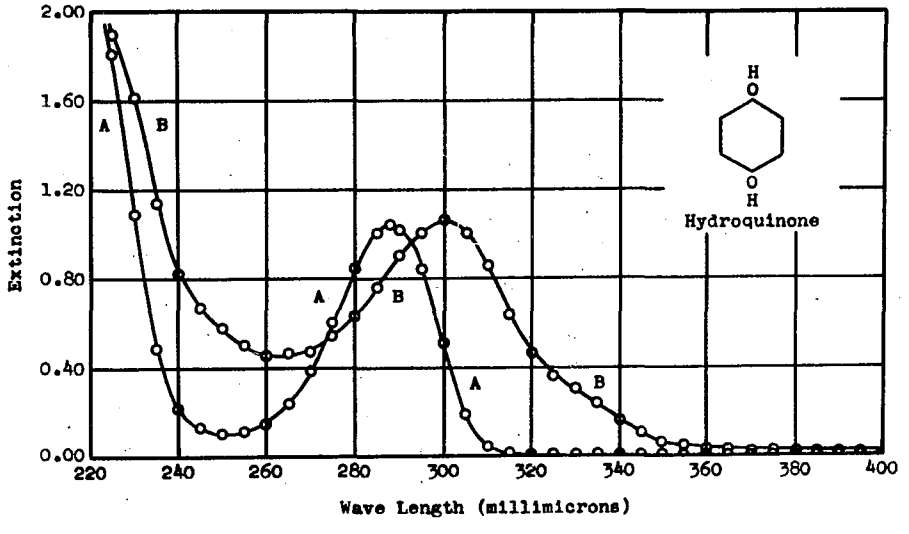

Figure 26. A-Hydroquinone (0.000045 g./ml.)
B-Hydroquinone (0.000045 g./ml.)
Potassium Sulfite Dihydrate (0.000090 g./ml.)

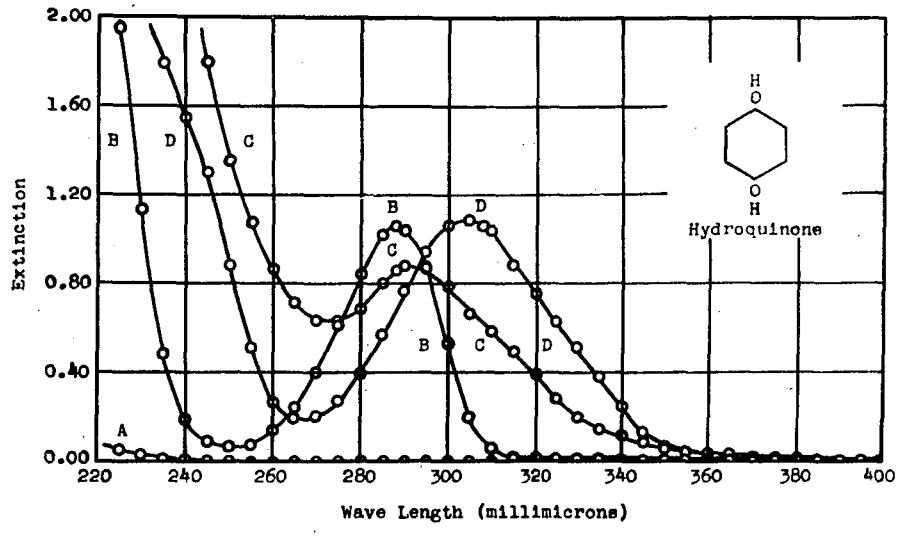

Figure 27. A. Cysteine Monohydrochloride (0.000090 g./ml.)
B. Cysteine Monohydrochloride (0.000090 g./ml.)
Hydroquinone (0.000045 g./ml.)
C. Cysteine Monohydrochloride (0.000090 g./ml.)
Sodium Carbonate (0.0002 g./ml.)
Hydroquinone (0.000045 g./ml.)
D. Hydroquinone (0.000045 g./ml.)
Sodium Sulfite (0.000090 g./ml.)

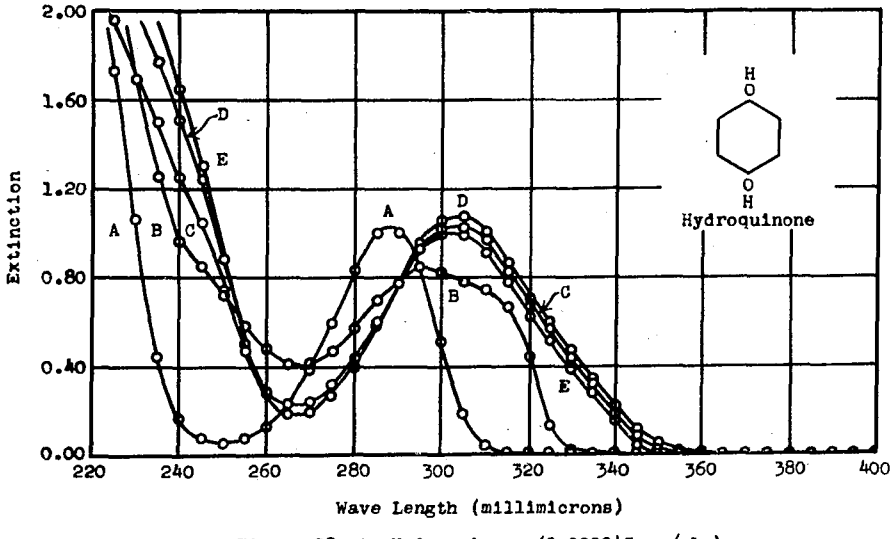

Figure 28. A. Hydroquinone (0.000045 g./ml.)
B. Hydroquinone (0.000045 g./ml.)
Sodium Sulfite (0.0000225 g./ml.)
C. Hydroquinone (0.000045 g./ml.)
Sodium Sulfite (0.000045 g./ml.)
D. Hydroquinone (0.000045 g./ml.)
Sodium Sulfite (0.000090 g./ml.)
E. Hydroquinone (0.000045 g./ml.)
Sodium Sulfite (0.000180 g./ml.)

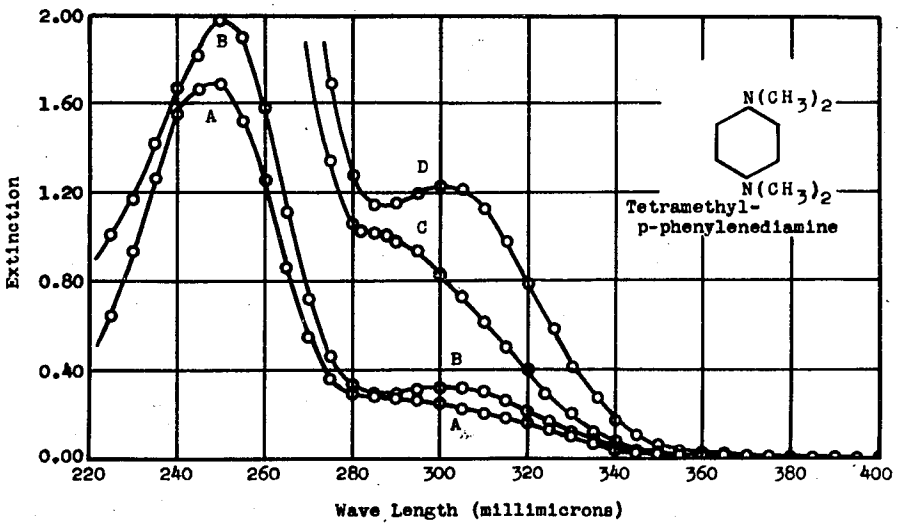

Figure 29. A. Tetramethyl-p-Phenylenediamine Dihydrochloride (0.000045 g./ml.)
B. Tetramethyl-p-Phenylenediamine Dihydrochloride (0.000045 g./ml.)
Sodium Sulfite (0.000090 g./ml.)
C. Tetramethyl-p-Phenylenediamine Dihydrochloride (0.000180 g./ml.)
D. Tetramethyl-p-Phenylenediamine Dihydrochloride (0.000180 g./ml.)
Sodium Sulfite (0.000360 g./ml.)

DISCUSSION

THE PROPERTIES OF SODIUM SULFITE

Since Stenstrom and Reinhard[1] in 1925 noted that sodium hydroxide decomposed hydroquinone before its ultraviolet absorption spectrum in alkaline solution could be determined, few,, if any, further investigations of hydroquinone in alkaline water solutions have been conducted. It is indeed fortunate that sodium sulfite is so diverse in its action that it allows hydroquinone and related compounds to exist in weakly alkaline solutions. Although sodium sulfite is only weakly alkaline, it can raise the pH of an aqueous hydroquinone from the acid to the alkaline side. If this compound did not possess any additional property, the hydroquinone would decompose rapidly since in the pH range 7.2 to 8.2, James, Snell and Weissberger[9] found that its autoxidation rate is very nearly proportional to the square of the hydroxyl ion concentration. However, sodium sulfite, the same sodium sulfite so commonly included in photographic developers as the preservative, has the property of inhibiting the autoxidation of hydroquinone and other dihydroxybenzenes, the aminophenols, phenylenediamines, and similar reducing agents. Since the breakdown of these compounds is accelerated by the presence of their oxidation products,

sodium sulfite is believed to act in the reduction of the oxidation rate by the removal of the oxidation products which are catalyzing the reaction[10]. Thus, it is evident that because of its oxidative inhibiting property the presence of sodium sulfite allows a study to be made of its effect on compounds that normally would decompose at corresponding pH values produced by a stronger alkali possessing no preservative effect.

THE CHARACTER OF THE SODIUM SULFITE EFFECT

The effect of sodium sulfite upon the dihydroxybenzenes, the aminophenols, and the phenylenediamines is at once evident from a study of Figures 1 through 9 or Table I. This agent causes a spectral shift to longer wave lengths of the ultraviolet absorption maximum of hydroquinone (Figure 1), of the p-aminophenol (Figure 4), and of the p-phenylenediamine dihydrochloride (Figure 7). The ortho and meta members of each of the three series show no spectral displacement of their absorption maxima. The extent of the shift to longer wave lengths for hydroquinone is 17 millimicrons; for p-aminophenol hydrochloride, 25 millimicrons; for p-phenylenediamine dihydrochloride, 20 millimicrons. In each case there is an increase in the intensity of the light absorption. Although it is true that each of these three compounds is a well-

known developing agent used in photographic developers, it does not follow that sodium sulfite causes a spectral shift with every developing agent. Both o-dihydroxybenzene (Figure 2) and o-aminophenol (Figure 5) exhibit developing activity[11], though less powerful than the corresponding para isomer. This applies also to o-phenylenediamine (Figure 8). It appears, therefore, that the effect of sodium sulfite is not one that can be correlated to developer activity but rather to the actual structure of the compound.

THE EFFECT OF SULFITE ON SUBSTITUTED BENZENE DERIVATIVES

The action of sodium sulfite on substituted p-disubstituted benzene derivatives is further illustrated by Figures 10-12. Elon or Metol (Monomethyl-p-aminophenol sulfate), Amidol (diaminophenol dihydrochloride), and Glycin (p-hydroxyphenyl glycin) show a shift to longer wave lengths in their ultraviolet absorption spectra upon the addition of sodium sulfite. Diaminophenol dihydrochloride shifts 25 milimicrons, Monomethyl-p-aminophenol sulfate and p-hydroxyphenyl glycin each shift 30 millimicrons. There is a hyperchromic shift in each case also. Again, each of these three compounds possess photographic developing activity and represent some of the most useful developing agents of today. However, it should again be emphasized that the sulfite effect is

based on structural reasons rather than coincidental developing activity.

Each of these last three compounds possess increased structural complexity from the parent compound, p-aminophenol. Diaminophenol differs from this parent compound in that it has an additional amino group ortho to the hydroxyl group. Although the extent of the spectral shift is the same for both compounds, the increase in the extinction value of the absorption is greater for the diaminophenol than for p-aminophenol upon the addition of sodium sulfite. Monomethyl-p-aminophenol sulfate has a methyl group substituted for an amino hydrogen; p-hydroxyphenyl glycin has a carboxymethyl group in place of the amino hydrogen. Since the unsubstituted p-aminophenol shows a bathochromic shift of 25 millimicrons and since each of the substituted p-aminophenols give a bathochromic displacement of 30 millimicrons, itis evident that the methyl group and the carboxymethyl group when substituted on the amino group in place of a hydrogen give an increased bathochromic effect of 5 millimicrons.

A possible explanation of the above observed difference might be contained in the availability of the electrons in the resonance structures of the amino group in both cases. The amino group, possessing an unshared pair of electrons, is a group that releases electrons to the

benzene ring[12]. The methyl group, as shown by electrical measurements, possesses a dipole with the carbon negative[13]. Thus, the monomethylamino group would possess greater electron-releasing tendency than the amino group due to the repulsive action on the electron pair of the amino nitrogen by the negative carbon atom of the methyl group. The explanation of the effect of the group $-NHCH_2COOH$ would have to involve the study of the group $-NHCH_2COO^-$ since the sodium sulfite-glycin solution is alkaline. The negative charge resulting from the ionization would greatly intensify the electron-releasing power of the nitrogen of the amino group. Apparently, the increased freedom or availability of electrons for resonance is a prerequisite for increased bathochromic effects by the sodium sulfite.

EFFECT OF SULFITE ON VARIED BENZENE DERIVATIVES

Since many investigators have investigated the effect of alkali on phenol and reported a bathochromic shift, a comparison with the effect of sodium sulfite on this compound would be instructive (see Figure 13). The ultraviolet absorption spectrum of phenol fails to show a spectral shift in a solution of sodium sulfite of the same concentration that produces the shift in hydroquinone solutions. Evidently, the other para substituted hydroxyl

group is essential before a phenolic compound will be affected by sodium sulfite.

As mentioned previously, the carbon atom in a methyl group joined to a ring carbon atom is the negative end of a dipole and the loosely-held electrons of the carbon atom of the methyl group are attracted by the ring carbon atom. This loss of electrons to the ring is somewhat akin to the action of the nitrogen atom of the amine group and the oxygen atom of the hydroxyl group, both of which can and do furnish unshared electrons to conjugate with the ring carbon atom. Although the electron-releasing power of the amino and hydroxyl groups is greater than the methyl group, it would seem that a compound such as p-cresol would be somewhat the electronic equivalent of hydroquinone and should give the characteristic bathochromic shift of its absorption spectrum upon the addition of sodium sulfite. However, as shown in Figure 15, the addition of sodium sulfite to p-cresol fails to produce any spectral shift.

Further substitutions were then studied in which a part of the original substituent was retained instead of being replaced or displaced in its entirety. Hydroquinone diacetate (Figure 16) has a hydroquinone nucleus in which each hydrogen atom of the hydroxyl groups has

been replaced with a $-COCH_3$ group. This group has the net effect of making electrons less available to the ring. Apparently, this action is of such magnitude in its effect that the unshared electrons of the hydroxyl oxygen are not released to the ring as freely as in hydroquinone. Addition of sodium sulfite fails to produce a spectral shift in this substituted hydroquinone.

The substitution of a methyl group for the hydrogen of one of the hydroxyl groups of hydroquinone should, from what has been said before, increase the electron-releasing properties of the oxygen. This methoxy group still possesses electron-releasing powers as shown by the fact that it is an ortho-para orienting substituent, as is hydroxyl, in benzene substitutions but it does not have the power of the hydroxyl group. The addition of sodium sulfite to an aqueous solution of p-methoxyphenol produces no bathochromic effect on the ultraviolet absorption spectrum.

Para-phenylenediamine dihydrochloride undergoes a bathochromic shift of 20 millimicrons in its absorption spectrum when placed in a sodium sulfite solution. If one of the amino groups of this compound is combined to form the $-SO_2NH_2$ group, it might be presumed that since the $-SO_2-$ part of this group is highly electron-attract-

ing that there will be little chance for the amino group to furnish its unpaired electrons to the ring. This presumption is supported by the fact that the $-SO_2NH_2$ group is meta-orienting for substituents during substitution on the benzene ring. This action requires an effect on the ring which makes electrons less available. As seen from Figure 18, introduction of the $-SO_2NH_2$ group in place of one of the amino groups of p-phenylenediamine gives a compound which in the presence of sodium sulfite fails to give the 20 millimicrons bathochromic shift of the p-phenylenediamine itself.

THE POSSIBILITY OF COMPOUND FORMATION AS THE SULFITE EFFECT

Sodium sulfite does not react with aqueous solutions of hydroquinone. However, it does react with an oxidation product of this compound, namely, quinone, to give a colorless compound, hydroquinone monosulfonate[10]. As can be seen from Figure 14, the maximum of the curve representing the ultraviolet absorption of a quinone-sodium sulfite solution is at 310 millimicrons while the maximum for the hydroquinone-sodium sulfite solution occurs at 305 millimicrons. This similarity in absorption spectra caused some concern lest the sulfite effect be one of addition to hydroquinone in solution to give a mono- or disulfonate of hydroquinone. Such a compound formation

would result in a shift of the absorption spectrum to longer wave lengths[14].

However, to postulate the existence of hydroquinone mono- or disulfonate as the cause of the bathochromic spectral shift of hydroquinone upon addition of sodium sulfite is a highly improbable explanation. First, hydroquinone monosulfonate is a very weak developing agent[15] while hydroquinone-sodium sulfite solutions are active in developing photographic materials. It seems highly unlikely that an unused developer like the latter would contain a sufficient concentration of the sulfonates so as to affect the light absorption. Secondly, potentiometric titration of 100 millliliters of sodium sulfite (0.000090 grams per milliliter) by hydroquinone (0.000045 grams per milliliter), and the reverse titration, gave no results indicative of compound formation. Although not conclusive, this evidence would tend to support the conclusion that hydroquinone mono- or disulfonate formation does not occur in sufficient concentration so as to be a factor in the light absorption. Next, sodium sulfite could only form compounds through substitution on the benzene ring. The removal of the elementary oxidation products of developing agents is a process of compound formation between the oxidized form of the developing agent and sodium sulfite. Elon (Monomethyl-p-aminophenol sulfate), hydroquinone,

p-aminophenol, p-phenylenediamine, Amidol (diaminophenol dihydrochloride), Glycin (p-hydroxyphenyl glycin) as well as pyrocatechol and o-aminophenol form at least monosulfonates when their oxidation products are formed in sulfite-containing solutions[16]. If the effect of sodium sulfite was one of addition to the oxidation products of the various developing agents studied in this work with the result that the compound formed now is able to absorb light of greater wave length than before, then both pyrocatechol and o-aminophenol should give a bathochromic shift of some extent intheir ultraviolet absorption spectra. However, as we have already outlined, the absorption spectra of the o-disubstituted benzene derivatives that exhibit developing activity are unaffected by the addition of sodium sulfite, indicating that possible sulfonate formation has not occurred to a great degree.

There are also two further reasons indicating improbability of actual sulfite-organic compound combination into a formal compound. Sodium sulfite is a reducing agent that exhibits preservative action in aqueous solutions of photographic developers. Cysteine is a reducing agent that exhibits preservative action in aqueous solutions of photographic developers.[10] Both of these reducing agents act in the same manner, by the re-

moval of oxidation products through compound formation. Cysteine in the presence of quinone will give hydroquinone cysteine. As evidenced from Figure 27, cysteine monohydrochloride in an aqueous solution of hydroquinone does not give the bathochromic spectral displacement that sodium sulfite would have given had it been present.

Obviously, for compound formation as projected above to occur, a ring position must be free from substitution. Thus, sodium sulfite does not exhibit its preservative action on durohydroquinone since there is no ring position free from substitution[17]. It would exhibit little, if any, inhibiting action on such compounds as diaminodurene and tetrachlorohydroquinone. As can be seen from Figures 19-21, sodium sulfite solutions of these compounds undergo spectral shifts, apparently indicating no necessity of an unsubstituted ring position. Likewise, from Figure 29, it appears that complete methylation of both amino groups of p-phenylenediamine does not render the compound inactive to the action of sodium sulfite.

EFFECT OF SULFITE ON POLYSUBSTITUTED BENZENE DERIVATIVES

There is a change in the ultraviolet absorption spectrum of diaminodurene dihydrochloride upon the addition of sodium sulfite, as shown by Figure 19. A new maximum is formed at 295 millimicrons while the original

maximum at 270 millimicrons of the sulfiteless solution of the compound is retained. Tetrachlorohydroquinone undergoes a bathochromic shift from 305 to 328 millimicrons upon addition of sodium sulfite. There is a possibility that the halogens may be split off in alkaline solution but it is doubted that the pH was high enough for this action to occur. In both cases, however, there are apparently shifts to longer wave lengths with increased light absorption. But durohydroquinone, a compound very similar to diaminodurene, undergoes a shift to shorter wave lengths with a large increase in the intensity of light absorption (Figure 21). While the hypsochromic shift of durohydroquinone is of the extent of only 9 millimicrons, the hypsochromic shift of p-xylohydroquinone is 36 millimicrons. And yet the addition of another methyl group to p-xylohydroquinone to give the compound cumohydroquinone (Figure 22) renders this compound almost inactive to the action of the sodium sulfite, the magnitude of the bathochromic shift being only 2 millimicrons. Phloroglucinol (Figure 24) is not so highly substituted as the above discussed compounds but is a 1,3,5-trihydroxybenzene. Although this compound does not have two hydroxyl groups para to each other and although it is not a developing agent[18], its ultraviolet absorption spectrum is shifted by sodium sulfite to longer wave

lengths to the extent of 10 millimicrons.

The above stated facts do not lend themselves to clear interpretation. Both durohydroquinone and diaminodurene have a durene nucleus, and thus the methyl group moments would cancel in pairs. Since the small size of the amino (and hydroxyl) group does not give steric inhibition of resonance[19], the expected spectral shift would be to longer wave lengths as exhibited by p-phenylenediamine (and hydroquinone). Since the spectral activity is not as indicated it must be assumed that other mechanisms must be at work. It is possible that structural factors may inhibit or prohibit the action of the sulfite. The low solubility of polysubstituted benzene derivatives as well as the question of purity also tend to complicate the problem and add further questions as to the exact nature of the action of sodium sulfite on these complex molecules.

POSSIBLE SUBSTITUTES FOF SODIUM SULFITE

An extensive attempt was made to find a substitute for sodium sulfite that could produce a like action on the spectra of the various organic compounds studied. A logical starting point was to use another sulfite salt other than sodium. Potassium sulfite does give a bathochromic shift in the ultraviolet absorption spectrum of

hydroquinone, as would be expected (Figure 26). With hydroquinone, sodium bisulfite in a concentration equal to that of the sodium sulfite gives the usual spectrum that is associated with the hydroquinone alone. However, addition of sodium carbonate to the extent of 0.0001 gram per milliliter to insure complete dissociation of the bisulfite ion gives the spectral absorption characteristic of the sulfite ion on hydroquinone (see Figure 25).

Sodium arsenite, sodium hypophosphite, sodium phosphite, sodium nitrite, sodium selenite, sodium sulfate, Kodalk (sodium metaborate), and potassium metabisulfite, as well as selenious and phosphorous acids, were all tried unsuccessfully. In each case the organic compound was hydroquinone (0.000045 gram per milliliter) while the concentration of the inorganic compounds was 0.000090 gram per milliliter. It was concluded that only sodium sulfite, or a sulfite salt other than sodium, or a salt that can be converted in solution into sulfite ions, produces the spectral shifts observed upon its addition to the organic compounds capable of this action. Apparently, similarity of structure, as in the sulfite and selenite ions, is not a sufficient factor to produce spectral activity characteristic of the sulfite.

DISSOCIATION AND THE SULFITE EFFECT

The effect of pH on the spectra of various compounds has been thoroughly studied[1,2,3]. Increasing the alkalinity of a solution results in the ionization of ring hydroxyl and amino groups at definite values of the pH. The ionization of a hydroxyl or amino group would give a spectral shift to longer wave lengths, according to the rule of Doub and Vandenbelt[4]. The loss of a proton by either group would cause a negative charge on the group. The nature of this charge would enhance the electron-releasing power of the group and thus the electrons of the nitrogen would be more readily available for resonance structures. The spectral effect accompanying such loosening of the electrons is a shift of the maximum of the absorption spectrum to longer wave lengths.

Sodium sulfite does raise the pH of aqueous solutions of hydroquinone. A solution of hydroquinone (0.000045 gram per milliliter) has a pH of 6.7. Addition of sodium sulfite (0.000090 gram per milliliter) raises the pH to 9.1. This latter value is very close to 9.8. the value of the pK_1 of hydroquinone. The value of the pK_1 represents the pH value at which 50 per cent of the compound is dissociated. From these facts it is a possibility that sulfite may be causing the partial dissociation of hydroquinone. This in turn would give rise to a bathochromic

shift in the ultraviolet absorption curve of hydroquinone.

To test the validity of the above possibility requires raising the pH of a hydroquinone solution in the absence of sodium sulfite to the value of the pH in the presence of the sulfite. However, hydroquinone will not exist unchanged in aqueous solutions of that alkalinity. As mentioned previously, cysteine is a preservative agent superior to even sodium sulfite. Addition of cysteine monohydrochloride to hydroquinone solutions does not affect the spectral absorption of the hydroquinone (Figure 27), but due to the hydrochloric acid that is released, the pH is lowered. Hydroquinone (0.000045 gram per milliliter) in solution with cysteine monohydrochloride (0.000090 gram per milliliter) gives a pH value of 3.30. To raise the pH sodium carbonate (0.0002 gram per milliliter) is added to the solution of the above two constituents. The pH is thereby raised to 9.86. Even at this value which is equal to the pK_1 of hydroquinone, the absorption curve (curve C, Figure 27) has not shown the spectral shift shown at a pH of 9.1 in the presence of sodium sulfite. The curve of the hydroquinone-cysteine-sodium carbonate solution shows a reduction in light absorption as well as a small (two millimicrons) bathochromic shift. On the evidence discussed above it would seem that although some dissociation of the hydroxyl and amino groups may occur, this dissociation

is not the primary cause of the spectral shifts observed when benzene compounds containing these groups are placed in sulfite-containing solutions.

The alkalinity of the solution seems to be a critical factor, however. The addition of only 0.0000037 gram per milliliter of hydrochloric acid is sufficient to cause a hypsochromic shift of a hydroquinone-sulfite solution absorption spectrum to the spectrum characteristic of the hydroquinone alone. The effect of the hydrogen ions of the acid would tend to suppress the ionization of the ring hydroxyl groups. Although this effect and the lowering of the pH to 6.6 are effects of the acid, the further action of the hydrogen ions to convert the sulfite ions to bisulfite ions is the probable reason for the necessity of alkaline solution. It has already been demonstrated that sodium bisulfite is without effect on the absorption spectrum of hydroquinone (Figure 25).

THE EFFECT OF VARIATION IN THE CONCENTRATION OF SULFITE

The effect of varying the concentration of sodium sulfite while maintaining a constant concentration of hydroquinone was studied (Figure 28). The concentration of hydroquinone was 0.000045 gram per milliliter. When sodium sulfite of a concentration of 0.0000225 gram per milliliter is added to the solution of hydroquinone, the

absorption spectrum decreases in light absorption and shifts 7 millimicrons to longer wave lengths. This curve is characteristic of curves obtained during the breakdown of hydroquinone into varied oxidation products. The sodium sulfite is present in sufficient concentration to raise the pH from 6.7 to 7.1 but it is not present in sufficient concentration to exert adequate preservative action to prevent the increased oxidative rate caused by the higher alkalinity of the solution. A concentration of 0.000045 gram per milliliter of sodium sulfite gives a spectral absorption maximum at 300 millimicrons; a concentration of 0.000090 gram per milliliter gives a maximum at 305 millimicrons and the highest light absorption. Increasing the concentration of the sulfite to 0.000180 gram per milliliter gives an absorption maximum at 300 millimicrons but slightly decreased extinction values. Further increases of concentration of sodium sulfite up to 0.000540 gram per milliliter did not change the wave length value of the absorption maximum but the extent of the light absorption decreased slightly with increasing sodium sulfite concentration. As can be seen from Figure 28, the curves for hydroquinone-sulfite solutions have a similar form once that sodium sulfite has reached a concentration of 0.000045 gram per milliliter.

A similar series of sulfite concentration variations was run with p-phenylenediamine dihydrochloride. The p-phenylenediamine dihydrochloride had a concentration of 0.000045 gram per milliliter in each case. Sodium sulfite of a concentration of 0.000009 gram per milliliter did not affect the absorption spectrum of the p-phenylenediamine dihydrochloride which has a maximum at 285 millimicrons. Concentrations of sodium sulfite of 0.09, 0.0009, and 0.000090 gram per milliliter showed in each of the three cases a spectral shift of 20 millimicrons to 305 millimicrons. In the case of this more stable compound variation in the concentration of the sodium sulfite had no effect once a sulfite concentration had caused a shift in the ultraviolet absorption spectrum of the p-phenylenediamine dihydrochloride.

As shown by the above case, the spectral shift due to sodium sulfite does not occur until a certain concentration value is reached, then the absorption maximum characteristic of the organic compound shifts suddenly to a maximum value of both light absorption and extent of spectral displacement to longer wave lengths. With hydroquinone this value occurs when the sodium sulfite concentration is twice the concentration of the organic compound. Further increases of sodium sulfite concen-

tration fail to give any further bathochromic shift. The sudden shift at a definite sulfite concentration is somewhat similar in action to ionization at a definite alkalinity value, indicating that the specific action of sodium sulfite requires definite conditions before it occurs.

SUMMARY

A general rule regarding the sulfite effect can be formulated: The addition of sodium sulfite to aqueous solutions of disubstituted benzene derivatives, containing either hydroxyl or amino groups, will produce a bathochromic shift in the ultraviolet absorption spectra of only those compounds that have their substituents oriented para to each other.

Substitution of one amino hydrogen by a group enhancing electron transfer to the ring increases the extent of the bathochromic shift in substituted aminophenols.

The insulation of an amino group from the ring by an intervening group, an electron-attracting group, has the effect of making the absorption spectrum of the new compound impervious to the action of sodium sulfite.

The replacement of one or both hydrogen atoms of the hydroxyl groups of hydroquinone by methyl or acetate groups renders the compounds formed inert to the action of sulfite.

Complete methylation of both amino groups of p-phenylenediamine apparently does not inactivate the compound to sodium sulfite.

Although sodium sulfite combines readily with the

oxidation products of p-disubstituted benzene derivatives studied, compound formation has been shown not to be the explanation of the action of the sulfite.

Sodium sulfite causes both bathochromic and hypsochromic spectral shifts with polysubstituted benzene derivatives, structural and resonance factors probably determining the end result.

A sulfite salt other than sodium, or a salt convertible to sulfite ions in solution, are the only compounds of the many tried that resulted in the action characteristic of sodium sulfite itself.

The alkalinity of the solution alone has been shown to be unable to produce the spectral shift credited to action of the sulfite.

The spectral shift due to sodium sulfite does not occur until a certain concentration of sulfite is present, then the absorption spectrum maximum shifts to the maximum extent and thereafter the shift is not increased by increasing the concentration of the sulfite.

The sulfite effect, occurring even when the ring or amino substituents are completely blocked with methyl groups, appears to be an action in which the sulfite, either alone or in conjunction with the solvent, acts upon the p-substituted substituents to effect increased electron release by the oxygen and nitrogen atoms. Such

a loosening of the electronic structure would result in the absorption of light of greater wave length (and less energy) than would be possible if the sodium sulfite was not present.

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