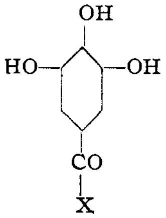
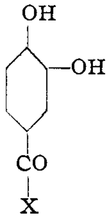
[COMMUNICATION NO. 787 FROM THE KODAK RESEARCH LABORATORIES]

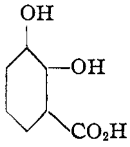
The Effect of Resonance on the Activity of Some Developing Agents

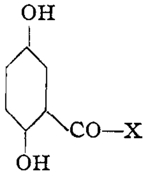
BY E. C. ARMSTRONG, T. H. JAMES AND A. WEISSBERGER

While gallacetophenone (I, X = CH_3), gallic acid esters (I, X = OR), and gallamide (I, X = NH_2) are developing agents similar to pyrogallol, gallic acid itself (I, X = OH), even under extreme conditions, develops only a very weak image.


I


II


III


IV

Similarly, protocatechuic ester (II, X = OR), protocatechuic amide (II, X = NH_2), and protocatechuic aldehyde (II, X = H) are described as developing agents of about the strength of pyrocatechol, while protocatechuic acid (II, X = OH) is not a developing agent. Homolka[1] pointed out that the fundamental difference between the acids on the one hand, and the acid derivatives, the ketone, and the aldehyde on the other, cannot be caused by the acidic function as such, because the corresponding sulfonic acids, though they are stronger than the carboxylic acids, act as developing agents under normal conditions. Homolka therefore suggested that an interaction exists between the carboxylic acid group and a hydroxyl group in the para position, so that gallic acid acts like resorcinol and protocatechuic acid like phenol. It was considered as further evidence for the specific relation between the hydroxyl and the carboxyl groups in the para position that *p*-hydroxybenzoic acid has a dissociation constant lower than that of benzoic acid, while *o*- and *m*-hydroxybenzoic acids have higher dissociation constants. Homolka found further that 2,3-dihydroxybenzoic acid (III) develops the latent image in alkaline solution just as well as pyrocatechol,[2] and he therefore concluded that the carboxylic acid group does not interfere with a hydroxyl group if the latter is in the ortho position.

When derivatives of hydroquinone were prepared in connection with other work, hydroquinone carboxylic acid (gentisic acid) (IV, X = OH) was tested in order to see whether it is an active developing agent under normal conditions. This was found not to be the case. Gentisic acid is too inactive to allow a test when used in a carbonate alkaline developer. When a developer with caustic alkali was employed and silver chloride paper was used as the photographic material, the development rate was found to be only about one-tenth of that with *hydroquinone monosulfonic* acid under the same conditions. It is interesting to note that the rate of oxidation by molecular oxygen was too small to measure accurately at *p*H 8.04, *i. e.*, more than one thousand times smaller than that of hydroquinone itself under the same conditions. This shows that the inactivity of gentisic acid, and presumably that of gallic acid and of protocatechuic acid, are not limited to the specific conditions of photographic development.

The inactivity of gentisic acid suggests a paralyzing action of the carboxylic acid group on the hydroxyl group in the ortho position, in disagreement with the earlier result on the 2,3-dihydroxybenzoic acid. The latter acid was therefore prepared and submitted to a test. When used in a standard carbonate–sulfite developer, the compound gave no trace of development in three hours. Catechol in the same formula gave about the same rate of development as hydroquinone. When 2,3-dihydroxybenzoic acid was used in the following formula

Agent	$-0.01\ M$	Phenosafranin	$-0.0001\ M$
Na_2CO_3	$-0.15\ M$	NaOH	$-0.01\ M$

in the absence of oxygen, an image appeared after about two hours. Comparative rates of development by catechol and 2,3-dihydroxybenzoic acid under the same conditions are as follows.

TABLE I

SLOPE OF THE TIME/DENSITY CURVE

	7th Step	11th Step
Catechol	0.44	0.25
2,3-Dihydroxybenzoic acid	0.002	0.0015

Accuracy of determinations with 2,3-dihydroxybenzoic acid was impaired by heavy stain and the necessity for long times of development.

These experiments show that 1,2-dihydroxyben-

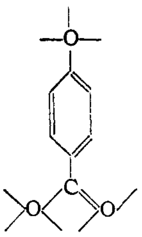
---

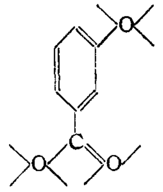
[1] Homolka, *Phot. Korr.*, **56**, 387 (1919).

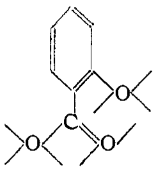
[2] Ref. 1, p. 391.

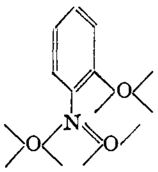
zene is very strongly paralyzed as a developing agent by the introduction of a carboxylic acid group in position 3. The behavior of protocatechuic acid, of 2,3-dihydroxybenzoic acid, and of gentisic acid might be accounted for if a hydroxyl group in the ortho or in the meta position had been masked by the carboxylic acid group. However, an effect on a hydroxyl group in the meta position would not explain the inactivity of gallic acid, and we conclude that a carboxylic acid group masks a hydroxyl group both in the para and in the ortho position. As a mechanism for the inactivation of the hydroxyl group in the para and in the ortho position, the following is suggested.

It is well known that compounds of the dihydroxybenzene type are active as reducing agents in the form of their ions, in which the hydroxyl groups are ionized. If a hydroxybenzene monocarboxylic acid undergoes electrolytic dissociation, both the carboxylic acid group and the hydroxyl groups may become dissociated. In the first step the carboxylic acid group will dissociate almost exclusively on account of its greater acidic strength. Then the hydroxyl groups will ionize. The ions thus formed may have the configurations V, VI or VII

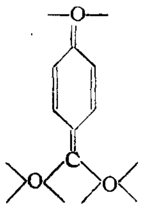

V ·

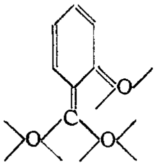

VI

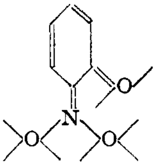

VII


VIII

where — indicates two electrons. V might also be written as Va, and VII as VIIa


Va


VIIa


VIIIa

while no corresponding second formulation of VI exists. Therefore, the ions V and VII will, according to the theory of resonance,[3] exist as hybrids between V and Va, and between VII and VIIa. This will stabilize the ions and make them less reactive, and a *carboxylic* acid group in the para or in the ortho position to a hydroxyl group will have a masking effect on the latter which is not exerted upon a hydroxyl group in the meta position. A *sulfonic* acid cannot have a double bond between the sulfur atom and the carbon atom to which the sulfur atom is attached, and therefore no forms corresponding to Va and VIIa are possible with phenolsulfonic acids. The inactivating influence of the sulfonic acid group in developing agents in the ortho and in the para position to a hydroxyl is smaller than that caused by the carboxylic acid group in gallic acid, protocatechuic acid, 2,3-hydroxybenzoic acid, and gentisic acid. It appears to be caused largely by the additional negative charge of the active anion, which is contributed by the acidic substituent. No such effect is expected with *nitro* compounds, *e. g.*, with nitrohydroquinone. However, this compound is described by A. and L. Lumière and Seyewetz[4] as a developing agent of only about the strength of hydroquinone monosulfonate. At a *p*H of 10.6 and in the absence of sulfite, nitrohydroquinone develops according to our tests at about one-twentieth the rate of hydroquinone. A rate comparison of nitrohydroquinone and hydroquinone monosulfonate is difficult because the two compounds do not yield the same type of H. and D. curves. The monosulfonate reacts as a trivalent ion and developers made up with it therefore show large induction periods. Nitrohydroquinone starts development sooner than the hydroquinone monosulfonate, but beyond the induction period the rate of development with the nitro compound is only one-half to one-third as great as that with the sulfonate. Hence, if the charge effect which is caused by the dissociation of the sulfonic acid group is discounted, the nitro group has an appreciably greater depressing effect upon the development rate than the sulfonic acid group. This great influence of the nitro group may be due to the fact that a double bond can exist between the nitrogen and the carbon, VIIIa, and that resonance between the ions VIII and VIIIa depresses the activity of nitrohydroquinone as a developing

---

[3] Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940.

[4] A. and L. Lumière and Seyewetz, *Brit. J. Phot.*, **61**, 341 (1914).

agent. This resonance is indicated by the intense color which is formed immediately when the solution of nitrohydroquinone is made alkaline, even in almost complete absence of oxygen.

Brief mention is necessary in view of Homolka's reference to the dissociation constants of the hydroxybenzoic acids. Resonance between V and Va, and VII and VIIa would not explain a specifically low value of the dissociation constant of *p*-hydroxybenzoic acid. However, the dissociation constant of this compound cannot in fact be considered as specifically low, because it is practically identical with that of the corresponding methoxy compound, anisic acid.

The following *derivatives of hydroquinone*, the developing properties of which have not been described in the literature, were also studied in order to check the analogy with the derivatives of pyrogallol and of pyrocatechol: gentisic aldehyde (IV, X = H), its oxime, gentisic aldoxime, gentisic acid methyl ester (IV, X = OCH_3), and gentisic acid amide (IV, X = NH_2).

The developing properties of these compounds were tested in the following formula, which gave a *p*H of about 10.6:

Developing agent	0.01 *M*	Na_2CO_3	0.15 *M*
Na_2SO_3	0.125 *M*	KBr	0.0034 *M*

Development was carried out at 20° (68°F.) in an apparatus already described.[5] The photographic material was a normal motion picture positive emulsion and exposures were made on the Eastman IIb sensitometer. Agitation during development was supplied by unpurified cylinder nitrogen. The rates of oxygen oxidation were determined as previously described,[6] and are expressed as first-order constants. For these measurements, the solution was buffered at *p*H 8.04 by means of the phosphate system, and no sodium sulfite was added. Table II gives the rate data. The rates of development are expressed in terms of the slopes of the time–gamma curves at γ = 1.5 (column 2), the slopes of the time–density curves of the seventh step at D = 1.5 (column 3), and the slopes of the time–density curves of the eleventh step at D = 0.75 (column 4).

TABLE II

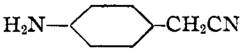
DEVELOPMENT AND OXYGEN OXIDATION RATES

	Rate: Gamma	Rate: D_7	Rate: D_{11}	Rate: oxygen oxidation
Hydroquinone	0.105	0.24	0.165	0.0175
Gentisic aldehyde	.0375	.077	.0475	.0012
Gentisic aldoxime	.06	.13	.085	.0061
Gentisic acid amide	.094	.205	.132	.0103
Gentisic acid methyl ester	.0445	.083	.055	.0010

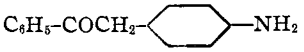
Table III summarizes some of the data for these developers.

These hydroquinone derivatives give good developers and are quite similar to hydroquinone in their action. Gentisic aldehyde yields a yellow stain, but the others do not. The density and gamma curves for the various developing agents are all of the same form, and may be nearly superimposed by proper adjustment of the time units. The aldoxime and acid amide yield practically the same H. and D. speeds as hydroquinone, while the methyl ester and aldehyde give from 10 to 20% less speed. The fog in every case is somewhat less than it is for hydroquinone, but not sufficiently less to constitute a significant improvement over hydroquinone. A comparison between the relative development rates and the relative oxygen oxidation rates (or better the square root of the oxygen oxidation rates) shows that a rough parallel exists between them. It is not to be expected, however, that the rates of development could be accurately determined from the rates of oxygen oxidation.

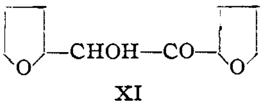
In addition, data may be given for *four compounds not obeying the Lumière–Andresen rules of structure*, which were found to show some developing ability. These compounds are: *p*-aminophenylacetonitrile (IX), phenyl 4-aminobenzyl ketone (X), furoin (XI), and dioxyacetone (XII)



IX



X



XI

$HOCH_2COCH_2OH$

XII

Phenyl-4-aminobenzyl ketone and *p*-aminophenylacetonitrile are two compounds which, by virtue of active methylene groups in the para position to an amino group, might be expected to oxidize rather easily to quinonoid systems. These compounds were found to develop Azo paper when used in the following formula

Agent	5 g.	Acetone	100 cc.
Na_2SO_3	10 g.	Water to make	1 l.
NaOH	5 g.		

---

[5] James, *J. Phys. Chem.*, **43**, 701 (1939).

[6] James, Snell and Weissberger, THIS JOURNAL, **60**, 2084 (1938).

TABLE III

COMPARISON OF DEVELOPERS OF THE HYDROQUINONE SERIES

Developing agent	Color of developing solution	pH deviation from hydroquinone	Av. relative developing rate	Sq. root of relative O_2 oxidation rate
Hydroquinone	Water	0.00	1.00	1.00
Gentisic aldehyde	Orange-brown	− .03	0.32	0.26
Gentisic aldoxime	Yellow	− .01	.54	.59
Gentisic acid amide	Light yellow	....	.85	.77
Gentisic acid methyl ester	Yellow	− .03	.36	.25

At 23°, *p*-aminophenylacetonitrile yielded a brownish image of moderate density within ten minutes, but the image was uneven and noticeable fog was produced. Much of the developing power of the solution had been lost after thirty minutes of contact with air. Phenyl 4-aminobenzyl ketone yielded a gray image of moderate density and low contrast within three minutes, but once more the image was uneven and the fog appreciable.

The fact that these compounds are developing agents provides interesting additional evidence in favor of the suggestion that the faculty for quinone formation is connected with the ability to develop the latent image.[7]

Furoin and dioxyacetone yielded some image development under special conditions, but in all cases heavy fog was obtained. The best results were achieved by a two-bath development process; the first bath contained the developing agent, and the second a buffer at *p*H around 9.0 to 9.5. The image was brown in color and in some instances could be removed by rubbing the wet film. Development was invariably uneven and appeared to be chiefly physical.

The materials employed in this investigation were as follows.

2,3-Dihydroxybenzoic acid was prepared according to German Patent 51,381 [*Frdl.*, 2, 133 (1887–1890)] and 281,214 [*Frdl.*, **12**, 683 (1914–1916)]; m. p. 204–206°.

Gentisic acid was prepared by oxidation of salicylic acid with persulfate, m. p. 201–203°.

Nitrohydroquinone was prepared from hydroquinone monobenzoate according to the procedure of Richter.[8] It forms bright red crystals of m. p. 130–131°.

Hydroquinone monosulfonate was identical with the material described by James and Weissberger.[9]

Gentisic aldehyde was prepared according to the procedure of Neubauer and Flotow,[10] as yellow needles, m. p. 100–101°.

Gentisic aldoxime was prepared in the usual way from the aldehyde and hydroxylamine hydrochloride in aqueous sodium hydroxide solution. After recrystallization from water it forms white needles, m. p. 120–121°.

Anal. Calcd. for $C_7H_7O_3N$: C, 54.9; H, 4.58; N, 9.15. Found: C, 54.64; H, 4.73; N, 9.17.

Gentisic acid methyl ester was prepared according to Graebe and Martz,[11] m. p. 85–86°.

Gentisic acid amide was prepared by treating gentisic acid methyl ester with ten times its weight of concentrated aqueous ammonia at room temperature for twenty-four hours. Recrystallized from water, it forms light-brown crystals, m. p. 216–217°.

Anal. Calcd. for $C_7H_7O_3N$: C, 54.9; H, 4.58; N, 9.15. Found: C, 54.41; H, 4.82; N, 9.03.

_p_-Aminophenylacetonitrile hydrochloride, furoin, and **dioxyacetone** were obtained from the Eastman Kodak Company.

Phenyl-4-aminobenzyl ketone was prepared from desoxybenzoin by the method of Golubew.[12] It forms white needles, m. p. 95–96°.

Summary

The developing activity and autoxidation rate of various derivatives of hydroquinone, some of which are new, and the developing activity of 2,3-dihydroxybenzoic acid were determined.

It was shown that the inactivation of developing agents of the type of di- and tri-hydroxybenzenes caused by the introduction of carboxylic acid groups or of nitro groups is largely due to the stabilization of the anions by resonance.

Four compounds which do not obey the Lumière–Andresen rules for the structure of developing agents were proved to have developing activity.

ROCHESTER, N. Y. RECEIVED SEPTEMBER 27, 1940

---

(7) Andresen, *Phot. Mitt.*, **28**, 124 (1891); Desalme, "Ve Congrès Internationale de Photographie," Brussels, 1910, p. 178; Abribat, *Bull. soc. chim.*, **29**, 265 (1921); Homolka, *Phot. Korr.*, **59**, 739 (1922).

(8) Richter, *Ber.*, **49**, 1401 (1916).

(9) James and Weissberger, THIS JOURNAL, **61**, 442 (1939).

(10) Neubauer and Flotow, *Z. physiol. Chem.*, **52**, 382 (1907).

(11) Graebe and Martz, *Ann.*, **340**, 214 (1905).

(12) Golubew, *Ber.*, **11**, 1939 (1878).