

[COMMUNICATION NO. 847 FROM THE KODAK RESEARCH LABORATORIES]

Oxidation Processes. XIV.¹ The Effect of Silver on the Autoxidation of Some Photographic Developing Agents

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The Ostwald-Abegg theory² of photographic development suggested that the developing agent reduces silver ions which are in solution. The silver ions may be added to the developer (physical development) or may come from the silver halide of the emulsion which dissolves as development proceeds (chemical development). The reduction comes to a standstill, for thermodynamic reasons, wherever a certain supersaturation of the silver atoms is reached in the emulsion. Silver specks, however, which are formed by the exposure of the silver halide to light act as crystallization nuclei. In their neighborhood the supersaturation is broken and the reduction continues. This theory obviously applies only to developers which form reversible oxidation-reduction systems and fails to explain the action of the common organic, sulfite-containing, developers. Piper³ suggested a catalytic action of the latent image on the reduction process itself, and Sheppard,⁴ and Volmer⁵ explained the mechanism of this catalysis. Sheppard studied the effect of certain compounds on the induction period of development and suggested that the developing agent forms a complex with the silver halide which, in the presence of metallic silver, decomposes into silver and the oxidized developing agent. Volmer passed air through *N* carbonate alkaline solutions of a number of developing agents and found that the resulting discoloration was accelerated by the addition of colloidal silver. His results are shown in Table I. The figures state the number of seconds after which solutions without silver and solutions which contained 0.5 g. of colloidal silver in 5 ml. had about identical colors.

Taking the formation of color as a measure of the oxidation and drawing the analogy between oxidation by air and by silver ion, Volmer suggested that a similar catalysis is essential in

photographic development. Such a catalysis would, like the quinone catalysis,^{6,7,8} affect the reactivity of the developing agent directly. It would be unspecific with respect to the oxidizing agent, while the mechanism suggested by Sheppard⁴ is specific for the reduction of metal salts. Likewise specific for metal ions is the mechanism suggested by James,⁹ according to which the reduction of the silver ions is accelerated when the latter are deformed through adsorption to silver or because they are located at the interface of silver and silver halide. To complete this brief account¹⁰ it may be mentioned that the unexposed grains are, according to Sheppard,¹¹ protected by an adsorption layer of gelatin which becomes permeable for the developing agents when silver nuclei are formed in the exposure. According to Schwarz and Urbach,¹² the protection of the unexposed grains of the common emulsions against reduction consists in an adsorbed electrical barrier. This is, according to James, the more effective the higher the charge of the active species of the developing agent, while it does not function against neutral molecules of the *p*-phenylenediamine type.

In view of their importance for the theory of development, Volmer's experiments were repeated with a volumetric control of the oxygen absorption. This appeared advisable because a change in the rapidity of discoloration of a developer through the addition of colloidal silver may or may not indicate that the silver affects the autoxidation itself, *i. e.*, the reaction of the developing agent with oxygen. The formation of the colored reaction products takes place in later phases of the reaction, and it may well be that the silver accelerates the discoloration without speeding up the autoxidation proper. Moreover, it may be questioned whether the effect recorded by Volmer is big enough to be significant for photographic

(1) Part XIII, James and Weissberger, *THIS JOURNAL*, **61**, 442 (1939).

(2) Ostwald, "Lehrbuch der allgemeinen Chemie," 2nd Ed., (1893), II, 1, p. 1078; Abegg, *Arch. für wiss. Phot.*, **1**, 15, 109 (1899).

(3) Piper, *Brit. J. of Phot.*, **55**, 195 (1908).

(4) Sheppard, *Phot. Journal*, **59**, 135 (1919); Sheppard and Meyer, *THIS JOURNAL*, **42**, 689 (1920).

(5) Volmer, *Z. wiss. Phot.*, **20**, 189 (1921); *Phot. Korr.*, **58**, 226 (1921).

(6) James and Weissberger, *THIS JOURNAL*, **60**, 98 (1938).

(7) James, Snell and Weissberger, *ibid.*, **60**, 2084 (1938).

(8) Kornfeld and Weissberger, *ibid.*, **61**, 360 (1939).

(9) James, *ibid.*, **62**, 536, 1649, 1654 (1940); *J. Phys. Chem.*, **43**, 701 (1939); *ibid.*, **45**, 223 (1941).

(10) For detailed information see C. E. K. Mees, "The Theory of the Photographic Process," The Macmillan Co., New York, N. Y.

(11) Sheppard, *Phot. Journal*, **69**, 330 (1929).

(12) Schwarz and Urbach, *Z. wiss. Phot.*, **31**, 77 (1932); Schwarz, *Phot. Korr.*, **69**, Suppl. No. 5, 27 (1933).

TABLE I

	VOLMER'S RESULTS ^a						
	Pyrocatechol	Metol	Hydroquinone	Glycine	<i>p</i> -Aminophenol	Amidol ^b	Eikonogen
With silver	60	30	40	30	20	30	30
Without silver	160	60	100	80	120	140	60

^a Metol = *N*-methyl-*p*-aminophenol; Glycine = *N*-*p*-hydroxyphenylaminoacetic acid; Amidol = 3,4-Diaminophenol; Eikonogen = 1-Amino-2-hydroxynaphthalene-6-sulfonate.

^b Aqueous solution without addition of carbonate.

development, unless the size of the observed catalysis was depressed by the experimental technique used.

Materials^{12a} and Methods

Hydroquinone was recrystallized from water; catechol from benzene.

p-Aminophenol was sublimed in a high vacuum (0.003–0.004 mm.); m. p. 189°. *p*-Aminophenol oxalate was recrystallized twice from water, containing about 1% of oxalic acid, decolorizing with Nuchar. The filtered crystals were washed with water, alcohol, and ether; m. p. 224° dec. *p*-Methylaminophenol was precipitated from a concentrated aqueous solution of the sulfate by sodium carbonate, filtered and dried. It was then distilled *in vacuo* [140° (3 mm.)], recrystallized twice from benzene and washed with petroleum ether; m. p. 86–87°. *p*-Methylaminophenol sulfate was recrystallized from slightly acidulated water. No difference was found in the autoxidation between the free bases and the salts.

p-Hydroxyphenylaminoacetic acid (photographic glycin) was dissolved in aqueous carbonate, filtered from insoluble impurities, precipitated with acetic acid and washed with water and alcohol. *p*-Phenylenediamine was distilled *in vacuo* and kept as a solid cake, m. p. 140–141°, the surface of which was discarded in taking samples for measurements. *p*-Aminodimethylaniline sulfate was precipitated from an alcoholic solution of the freshly distilled free base with the theoretical amount of sulfuric acid, recrystallized from

50% methyl alcohol, and washed with methyl alcohol and ether. 2,4-Diaminophenol sulfate (amidol) was precipitated from an aqueous solution of the hydrochloride by sulfuric acid, recrystallized from water containing about 1% of sulfuric acid and washed with water, alcohol and ether.

The silver was prepared by reduction of silver nitrate with formaldehyde as described by Volmer.⁵

The buffers were made up with potassium phosphate, carbonate, borate, diethyl barbiturate, or hydroxide. Twenty-five milliliters of 0.2 molar standard solutions was adjusted to the desired pH by addition of nitric acid or potassium hydroxide. The type of buffer and the pH are indicated with the experimental results. The hydrogen-ion concentrations were measured with a glass electrode. For solutions of a pH above 9 a special electrode^{12b} was used to reduce errors caused by cations. These were further diminished by using potassium salts exclusively. The measurements were made on duplicates of the solutions actually oxidized.

The apparatus for measuring the reaction rates was that described in the preceding papers of this series.¹³ The reactions were run at 20.0 ± 0.02°, the volumes given for the oxygen absorptions were measured over water at this temperature and reduced to 760 mm.; the G. M. V. for these conditions is 24.6 l. Before the start of the reaction, the buffer was in the bottom part of the reaction vessel, the developing agent in slightly acidulated solution in the top chamber. The silver was added to the buffer, and, in the experiments in presence of halogen ion, this was also added to the buffer. In the experiments with addition of permanganate, the vessel with two top chambers⁹ was used.

Results and Discussions

A critical factor in autoxidations of high velocity is the supply of oxygen to the reaction mixtures. Unless this is fast enough to maintain a constant oxygen concentration in the solutions, it may become the limiting factor of the oxygen absorption. The capacity of an apparatus similar to the one used at present was tested by Weissberger, Mainz and Strasser¹³ in the autoxidation of benzoin. With this reaction no observations were made in the very beginning of the absorption, and it appeared desirable to characterize the capacity of the present apparatus more completely. This is done in the experiments recorded in Fig. 1. At shaking rates of 270 oscillations per minute and

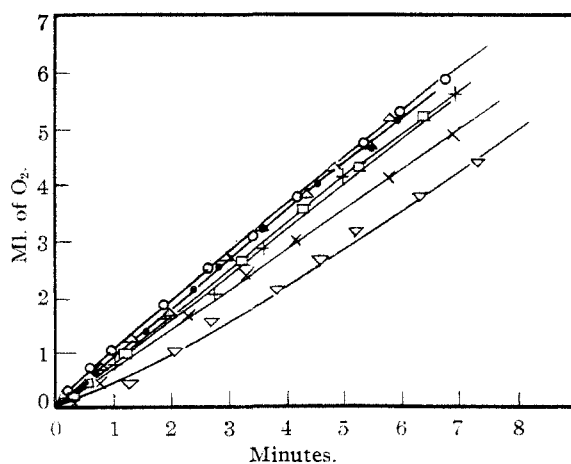


Fig. 1.—2 millimoles of hydroquinone in 50 ml. of 0.1 *N* barbital buffer, pH 8.06, with various shaking rates in oscillations per minute: O, 330 o.p.m.; Δ, 300; ●, 270; □, 240; +, 210; ×, 195; ∇, 180.

(12a) For the preparations we are indebted to Mr. E. C. Armstrong and Dr. John M. Snell.

(12b) National Technical Laboratories, Berkeley, California.

(13) Weissberger, Mainz and Strasser, *Ber.*, **62**, 1942 (1929).

higher, and absorption rates of 1 ml. per minute and lower, equilibrium between the gaseous (oxygen) and liquid phases is established. The critical shaking rates are somewhat higher with the new than with the old apparatus. Most likely the difference is due to the fact that in the older apparatus vigorous splashing of the solutions occurred at lower rates than in the new one. For reactions of high rates, the shaking mechanisms should cause jerky, rather than smooth, movements. In the experiments described in this paper, shaking rates of 280 o. p. m. were maintained. Hence, it will demonstrate a catalytic effect if the addition of silver raises the rate of the oxygen absorption from values up to 1 ml./min. to higher values. Rates, however, which are higher than 1 ml. oxygen/min. will suffer a depression by a lack of saturation of the liquid phase which is the more serious the higher the rate.

An insufficient saturation of the liquid phase with oxygen appears to be responsible for results published recently by Green and Branch.¹⁴ These authors claim that the rate of the autoxidation of hydroquinone is proportional to the $3/2$ power of the hydroxyl-ion concentration, and, on the basis of this result, draw conclusions about the mechanism of the reaction. The same rate law had been found by LaMer and Rideal,¹⁵ while it is contradicted by the results of Euler and Brunius¹⁶ and of Reinders and Dingemans,¹⁷ who found that the autoxidation rate is proportional to the square of the hydroxyl-ion concentration. James, Snell and Weissberger⁷ have confirmed this quadratic dependency. Green and Branch worked with solutions containing about 10 m. mole of hydroquinone and observed only the beginning of the autoxidation over a range where the uptake of oxygen per minute could be treated as constant. Plotting \log (ml. O_2 /min.) against pH , they obtained a straight line with the slope $3/2$. James, Snell and Weissberger, using 0.5 m. mole of hydroquinone for each run, followed the course of the oxygen absorption until it had slowed down considerably. They calculated the rate constants according to the first-order law, using as final volume absorbed the theoretical one of the reaction



When the logarithm of the rate constant was plotted against pH , a linear dependency was ob-

(14) Green and Branch, *THIS JOURNAL*, **63**, 3441 (1941).

(15) LaMer and Rideal, *ibid.*, **46**, 223 (1924).

(16) Euler and Brunius, *Z. physik. Chemie*, **139**, 615 (1928).

(17) Reinders and Dingemans, *Rec. trav. chim.*, **53**, 209 (1934).

tained with the slope 1.98. Following this procedure, with measurements made over a wider range of pH (6.95–8.21), the values of Fig. 2 marked by 0 were obtained. The straight line is drawn with a slope of 2.00, thus confirming the result of Euler and Brunius, Reinders and Dingemans, and James, Snell and Weissberger.

It might be contended that the use of the theoretical final volume in the calculation of the rate constants is arbitrary, although ample reasons exist for the validity of the above equation.^{6,7} To avoid this contention, the values of ml. O_2 /min. for each measured point of a number of experiments were plotted against the time, and the initial rates in ml. O_2 /min. were determined by extrapolation to time = 0. When these initial rates were plotted against pH , the values marked by X in Fig. 2 were obtained, which confirm that *the autoxidation rate of hydroquinone increases with the square of the hydroxyl-ion concentration*. The latter method of evaluation of the results is free from any assumption about the final volume and corresponds to that used by Green and Branch. The difference in the determination of the initial rates is necessitated by the fact that only 1/20 of the amount of hydroquinone used by Green and Branch was used in the present experiments in order to keep well within the limits of capacity of the apparatus.

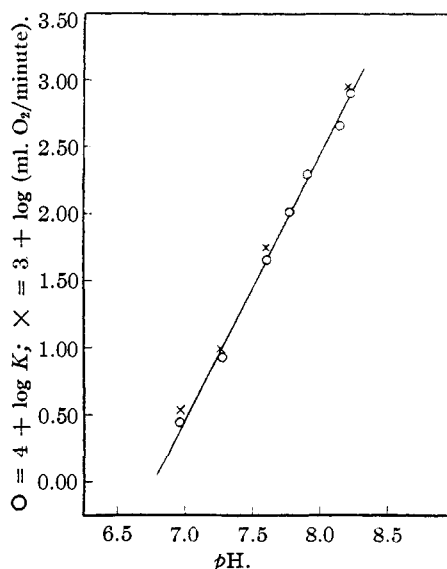


Fig. 2.—Dependency of rate of hydroquinone autoxidation on pH .

Experiments in the absence of silver with the concentrations and alkalinity used by Volmer proceeded at rates which were too high to maintain

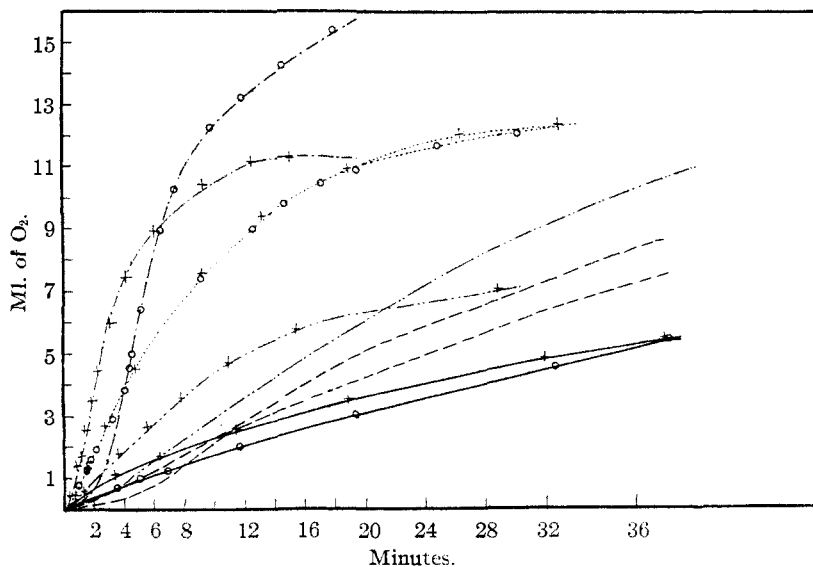


Fig. 3.—Reactions without silver, experimental points marked O; reactions with silver, experimental points marked +.

Line Style	Compound	pH	Buffer
—	Hydroquinone	7.98	Barbital
· · · · ·	Amidol	5.57	Phthalate
- - - - -	Glycine	7.50	Phosphate
· · · · ·	Glycine	9.18	Carbonate
- · - · - · -	<i>p</i> -Aminophenol	8.57	Borate

constant oxygen concentrations in the solutions. It may be mentioned, however, that in such experiments with catechol, metol, amidol and glycine no great increase in the rate of the oxygen absorption could be observed when silver was added. If it was the capacity of the apparatus which limited the effect in our experiments, the same might apply to Volmer's because the oxygen supply in our experiments was probably not less efficient than in those of this author. In order to obtain more exact data, buffered solutions containing 0.5 m. mole of the developing agents in 50 ml. were used. The pH's were so chosen that the absorption rates kept within the limits given above, and oxygen was used instead of air to keep the gas phase constant throughout the reactions. With each compound two experiments were made at the same pH, one of them with and the other without the addition of silver in a large excess (1.8 g. for each run). When silver is added to the reaction mixtures containing hydroquinone

(Figs. 3 and 4), the absorption of oxygen is accelerated only little in spite of the large excess of the metal and only in the beginning of the reactions. After an uptake of about 0.4 mole of oxygen per mole of hydroquinone, the absorption of the silver-containing solutions sinks below those of the corresponding silver-free systems, and the curves show that the silver decreases the total amount of absorbed oxygen. One might suspect that this deficit is caused by the presence of silver oxide which oxidizes part of the developing agent. However, analyses, for which we thank Mr. Ballard of these Laboratories, showed that the silver contained less than 0.4% of oxide. This can account for an oxidation of not more than 10% of the develop-

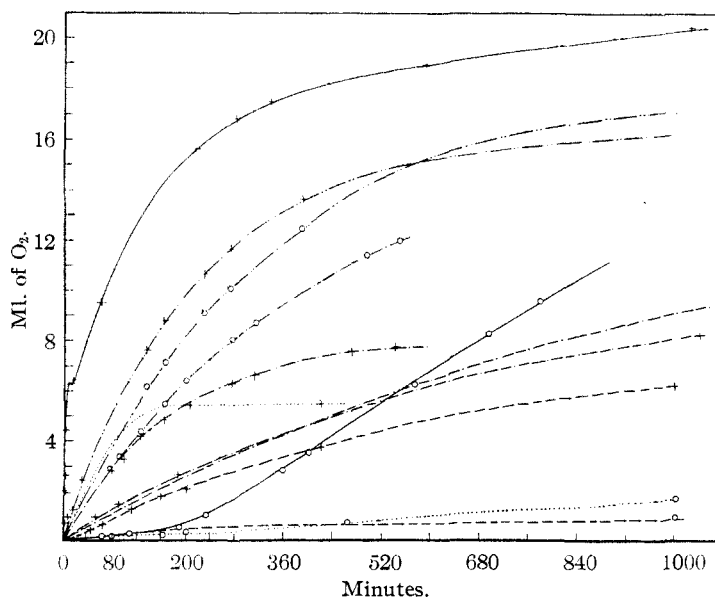


Fig. 4.—Reactions without silver, experimental points marked O; reactions with silver, experimental points marked +.

Line Style	Compound	pH	Buffer
—	<i>p</i> -Phenylenediamine	13.05	Potassium hydroxide
· · · · ·	<i>p</i> -Phenylenediamine	9.08	Borate
- - - - -	<i>p</i> -Phenylenediamine	7.57	Phthalate
· · · · ·	Metol	6.20	Phosphate
- · - · - · -	Catechol	8.40	Barbital
- - - - -	Hydroquinone	7.41	Phosphate

ing agent. The total absorption of oxygen by hydroquinone, however, may upon addition of silver drop as much as 25%, and that by other developing agents, *e. g.*, metol and *p*-aminophenol, even more than 50%.

A silver-catalyzed evolution of oxygen from peroxide (formed according to the above equation), is likely to contribute to the deficit. The catalytic action of silver on the decomposition of peroxide is well known.¹⁸ Table II illustrates the extent of this catalysis under the conditions of our experiments. It gives the times at which one half of the total oxygen evolution had taken place when solutions of 1 m.mole of hydrogen peroxide in 50 ml. of the various buffers were shaken at 20.0° with and without addition of 1.8 g. of silver. It is evident that hydrogen peroxide formed in the autoxidation will, in the presence of silver, decompose rapidly, and the liberation of oxygen contributes toward the deficit in the observed oxygen absorption.

pH	Times in minutes	
	Without silver	With silver
11.8	70	
11.7		0.1
7.9		1.4
7.6	21 × 10 ³	

Moreover, the reaction of hydrogen peroxide with the developing agent itself is catalyzed by silver. This is shown by the following experiments. One m.mole of hydrogen peroxide and 0.5 m.mole of hydroquinone in 50 ml. of 0.1 molar dipotassium phosphate of pH 7.5 were kept under nitrogen for twenty minutes. During this time, the volume of the gas phase did not change measurably. Then 20 ml. of 0.25 molar permanganate solution was added, and an evolution of 19.2 ml. of oxygen indicated that 78% of the peroxide was still present. In two corresponding experiments, but with addition of 2 g. of silver, the gas phase increased during the keeping period of twenty minutes by 0.6 and 1.2 ml., respectively, by the silver-catalyzed decomposition of the peroxide. In the absence of hydroquinone under otherwise identical conditions, this decomposition yields 5.5 ml. of oxygen. The reduction in the evolution of oxygen in the presence of hydroquinone is caused by a reaction of the hydroquinone with the hydrogen peroxide, which is catalyzed by the silver; when permanganate solution was added

(18) McIntosh, *J. Phys. Chem.*, **6**, 15 (1902); Wiegell, *Z. physik. Chem.*, **A143**, 81 (1929).

to the solutions which had evolved 0.6 and 1.2 ml., no further evolution occurred, showing that the peroxide had been used up completely. The observation that the deficit in the total oxygen absorption of the developing agents, which is caused by the presence of silver, varies with the different developing agents shows that the silver-catalyzed reaction between peroxide and developing agent takes place to a considerable degree. In the absence of silver, most of the peroxide appears to react with the quinonoid oxidation products of the developing agents.^{6,7}

Oxidation by silver oxide contaminating the silver will produce oxidation products of the developing agents and thus accelerate the autoxidation of those compounds which are subject to quinone catalysis.^{6,7} This acceleration is, however, not caused by a catalytic action of the silver. On the other hand, the consumption of developing agent by the silver oxide and by the silver-catalyzed reaction with hydrogen peroxide diminishes the amount of autoxidizable material, and, therefore, the rate of the oxygen absorption. This apparent rate of autoxidation is likewise diminished by the liberation of oxygen in the silver-catalyzed decomposition of hydrogen peroxide.

In Figs. 3-5, the absorption of oxygen is plotted against the time for pairs of experiments with

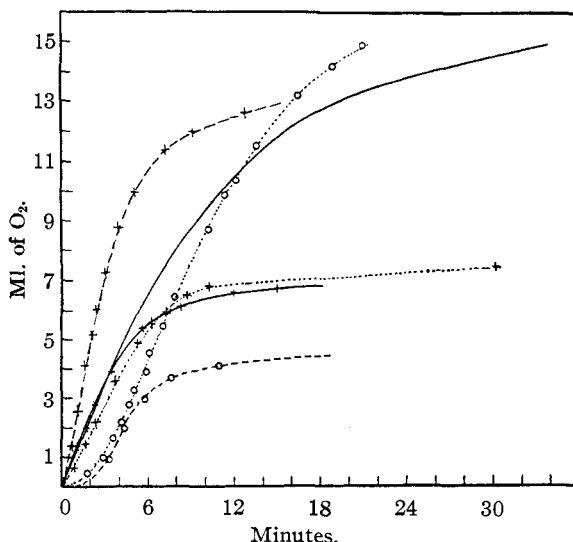


Fig. 5.—Reactions without silver, experimental points marked O; reactions with silver, experimental points marked +.

Compound	pH	Buffer
—	7.66	Phosphate
...	9.23	Borate
- - -	13.2	Potassium hydroxide

and without silver. In view of the badly defined end-points of many of the reactions, the calculation of rate constants does not afford an advantage for the interpretation of these data. The discussion will, therefore, be based upon an inspection of the curves themselves. The figures show that the silver accelerates the initial oxygen absorption of hydroquinone, catechol, *p*-aminophenol and glycine. The absence of an observable induction period with hydroquinone⁷ and catechol¹⁹ makes it unlikely that with these compounds the acceleration can be attributed to the elimination of an induction period. The latter effect is unmistakable in the cases of *p*-aminophenol and glycine, where it causes at least part of the observed speeding-up of the oxygen absorption. With metol and amidol no absolute acceleration of the oxygen absorption was observed on addition of silver. However, considering the above-mentioned simultaneous reactions as they are evidenced by the deficit in the total oxygen absorption, silver may cause some acceleration in the autoxidation of metol, while hardly any influence of the silver can be observed with amidol at *pH* 5.57. The total absence of an effect with amidol may be due to the low *pH* of the measurement. With all the other systems, the silver causes some small acceleration. It has not been studied whether the effect is limited to silver or whether it can likewise be caused by other metals. The latter is rather probable,⁶ but the effect is not general for fine powders as such, because the addition of purified diatomaceous earth had no effect at all.

The *pH* of our experiments with catechol, *p*-aminophenol, glycine and amidol included regions in which these developing agents can be used in practical development. With hydroquinone and metol the *pH* for the measurements had to be lower in order to keep the rates within the capacity of our apparatus. However, observations at different *pH* leave little doubt that at higher *pH* the influence of the silver would not show a significant increase. Hence, *no silver catalysis which is likely to be of importance for photographic development is observed in the autoxidation of the above-mentioned developing agents.* The acceleration of the rate of the darkening of these developing agents beyond that of their autoxidation in the presence of silver must be caused by an effect of the metal on other reactions than the autoxida-

tion proper. The colored compounds are formed by polymerization of the oxidized developing agents, and the silver-catalyzed oxidation of the developing agents by hydrogen peroxide may explain a certain amount of the darkening in Volmer's experiments. Moreover, the reaction of the hydrogen peroxide with quinonoid oxidation products of the developing agents in the absence of silver may be responsible for a decreased formation of dark products if the metal is not present.

Volmer did not include in his investigation *p*-phenylenediamine or its derivatives. It is these compounds, however, which show a marked effect of silver on their autoxidation. This is demonstrated in Figs. 4 and 5. With *p*-phenylenediamine the acceleration is about 10² fold; with *p*-aminodimethylaniline it is less, but still pronounced. The curve of the silver-catalyzed autoxidation of *p*-phenylenediamine at *pH* 13.05 has a marked and reproducible inflection after an absorption of about 1/2 equivalent of oxygen. In the beginning of the reaction, the concentration of hydrogen peroxide builds up, while that of the oxidized compound sinks, and conditions can be reached where the liberation of oxygen from peroxide just compensates for the absorption of oxygen by the developing agent. In certain other cases even a temporary increase in the oxygen volume was observed. The fact that a considerable catalytic action of the silver is limited to a certain type of the developing agents shows that neither an adsorption of oxygen to the silver nor the intermediary formation of silver oxide²⁰ gives a sufficient explanation for this catalysis. Such a mechanism might, however, be considered in connection with the small acceleration of the oxygen uptake by the developing agents of the types of hydroquinone and aminophenol. The lack of a silver catalysis with hydroquinone agrees with the results of Perry, Ballard and Sheppard²¹ who, disproving observations of Rabinowitsch,²² showed that this compound is not adsorbed to silver to any measurable extent. It would be interesting to see whether *p*-phenylenediamine is adsorbed to a higher degree.

The systems described above differ from developing emulsions by the absence of halogen ion. Addition of chloride ion depressed the effect of the

(20) Benton and Drake, *ibid.*, **56**, 255 (1934); Benton and Bell, *ibid.*, **56**, 501 (1934).

(21) Perry, Ballard and Sheppard, *ibid.*, **63**, 2357 (1941).

(22) Rabinowitsch and Peissachowitsch, *Z. wiss. Phot.*, **33**, 94 (1934).

(19) Joslyn and Brauch, *This Journal*, **57**, 1779 (1935).

silver on *p*-phenylenediamine. With the other developing agents it eliminated the effect of the silver on the total oxygen absorption, showing that the halogen ion interferes with the silver catalysis of the decomposition of hydrogen peroxide and of the oxidation of the developing agents by hydrogen peroxide. The effect of halogen ion on the shortening of the induction period, *e. g.*, of metal, is much less pronounced.

According to the present results, a catalytic effect of silver in photographic development of the type suggested by Volmer, *i. e.*, a catalysis which directly affects the reactivity of the developing agents is most unlikely with developing agents of the types of dioxybenzene and aminophenol. It may possibly play some role in development with *p*-phenylenediamine and its derivatives. For the discrimination between exposed and unexposed grains in general, however, the other mechanisms indicated in the introductory remarks should be responsible.

Summary

1. The oxygen absorption of hydroquinone at various rates of shaking was investigated to

check the conditions under which the concentration of oxygen in the liquid phase remains constant.

2. In agreement with results in earlier papers of this series and in disagreement with Green and Branch, it was shown that the rate of autoxidation of hydroquinone between *pH* 7 and 8.2 increases with the square of the hydroxyl-ion concentration.

3. Silver accelerates the autoxidation of hydroquinone, catechol, *p*-aminophenol, and glycine only to a very small degree. With these developing agents, therefore, the catalysis suggested by Volmer is most unlikely to be of significance for photographic development.

4. The autoxidation of *p*-phenylenediamine and *p*-dimethylaminoaniline shows a more considerable catalysis by silver.

5. The addition of silver strongly diminishes the total amount of oxygen which is absorbed by the developing agents in alkaline solutions. This is chiefly caused by a catalytic effect of the silver on reactions of peroxide formed in the autoxidation.

ROCHESTER, N. Y.

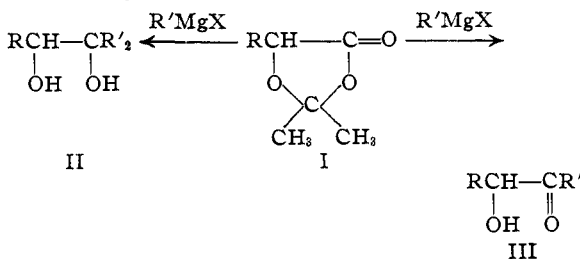
RECEIVED MARCH 10, 1942

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

Reductive Cleavage of Dioxolones by the Grignard Reagent

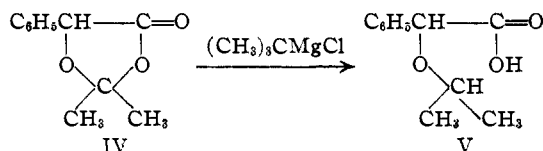
BY REYNOLD C. FUSON AND A. I. RACHLIN

Dioxolones, acetone derivatives of α -hydroxy acids (I), are known to react with the Grignard reagent to form glycols (II).¹ It seemed probable that if the reagent had a very highly branched radical, acyloins (III) might be produced.



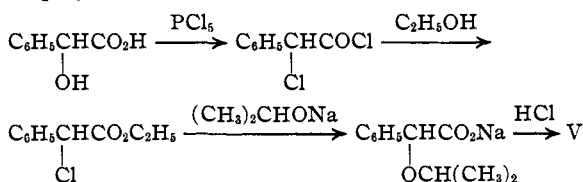
In an attempt to obtain the latter type of compound, the acetone derivative of mandelic acid (IV) was treated with *t*-butylmagnesium chloride. The product was not the acyloin, however, but α -isopropoxymandelic acid (V). Isobutylene was evolved.

(1) Freudenberg, Todd and Seidler, *Ann.*, **501**, 210 (1933).



The reaction is a hydrogenolysis of the dioxolone ring and appears to be new in type. Moreover, it has no parallel among the reactions between the Grignard reagent and esters or lactones.

The structure of the product was established by synthesis. The following series of reactions was employed



It has been found that the reaction is general for acetone derivatives of α -hydroxy acids. The iso-