Mechanism of Photographic Development. III. Developing and Non-Developing Reducing Agents

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A rather wide assortment of reducing agents can act as photographic developers. Among the many developing agents to be found in the literature are the following: hydroquinone, p-aminophenol, p-phenylenediamine, trioxymesitylene, ascorbic acid, 1-phenyl-3-methyl-4-amino-5-pyrazolone, hydrocoerulignone, quinoxaline, hydroxylamine, hydrogen peroxide, hydrazine, ferro-oxalate ion, molybdo-oxalate ion, sodium hydrosulfite, and possibly ferrous ion itself. Not all of these agents possess the power of selective action to the same degree. Hydrazine and sodium hydrosulfite, for example, are notably poor developing agents, and quinoxaline will yield an image only under special conditions. Certain other agents are capable of reducing silver halide to metallic silver, but are not developers, since they yield the same result whether or not the sensitive layer has been exposed to light. The best known member of this group is sodium stannite. Sodium sulfite demands special consideration, since it is thermodynamically capable of reducing silver chloride, but fails to do so under ordinary processing conditions. Any general theory of developer action must be able to explain not only the developing action of a wide assortment of reducing agents, but also the lack of developing action on the part of certain other agents.

The most important characteristic of the usual developing agent is its ability to reduce the exposed silver halide grains at a substantially greater rate than the unexposed. An understanding of the basis for this difference in rate is evidently of major importance to the theory of development. It is notable that, in every case sufficiently examined, a definite silver catalysis of the reduction of silver ions by the developing agent exists, although the mere existence of such catalysis does not assure developing power. The reducing agents known to show such silver catalysis are the following: hydroquinone,[1,2] hydroxylamine,[3,4] p-

phenylenediamine,[5] p-aminophenol,[6] catechol,[6] ascorbic acid,[6] hydrazine,[7,8] and sodium sulfite.[9] Of this list, the first six compounds are good developing agents, hydrazine is a very poor developing agent, and sodium sulfite does not develop at all. The case of hydrazine has already been considered in some detail.[8] In the present paper, the behavior of sodium sulfite, sodium stannite, furoin and desylamine will be examined.

Sodium Sulfite.—Sheppard[9] has pointed out that the formation of metallic silver in a silver nitrate–sodium sulfite solution is strongly catalyzed by colloidal silver, but even the catalyzed process occurs only very slowly at room temperature. At 50–60°, however, the reaction rate can be followed conveniently by methods already described.[2,5] In the present work, a Carey Lea dextrin reduction silver sol was usually employed as catalyst with gum arabic as stabilizer. Some check experiments were made with a silver sol freshly prepared by hydrazine reduction of silver ions in the presence of a gold nuclear sol, and a silver sol obtained directly from the silver nitrate–sodium sulfite–gum arabic system. The results were qualitatively the same. Figure 1 shows the type of curve obtained in the presence of the catalyst.

Although the present results are only of semi-quantitative value, they show clearly that the rate of formation of silver is dependent upon the silver-ion concentration. This is evident from the data in Table I. The rates given in the column marked "R*" are in terms of the slopes of the time–density curves at $D = 1.0$; "t^*" gives the time (in minutes) required to obtain a density of 0.2. A comparison of the data of the last two columns shows that, if we assume that the reaction rate is proportional to the sulfite-ion concentration, it is likewise proportional to about the 0.75 power of the silver-ion concentration; a result which is understandable if adsorption of silver ions to silver is involved. The silver-ion concentrations are calculated on the basis of a disso-

(1) R. Livingston and J. J. Lingane, *J. Chem. Education*, **15**, 320 (1938).

(2) T. H. James, THIS JOURNAL, **61**, 648 (1939).

(3) S. E. Sheppard and C. E. K. Mees, "Investigations of the Theory of the Photographic Process," Longmans, Green and Co., New York, N. Y., 1907, p. 151 ff.

(4) T. H. James, THIS JOURNAL, **61**, 2379 (1939).

(5) T. H. James, *J. Phys. Chem.*, in press.

(6) Unpublished work.

(7) K. Jablczynski and S. Kobryner, *Roczniki Chem.*, **9**, 715 (1929).

(8) T. H. James, THIS JOURNAL, **62**, 1654 (1940).
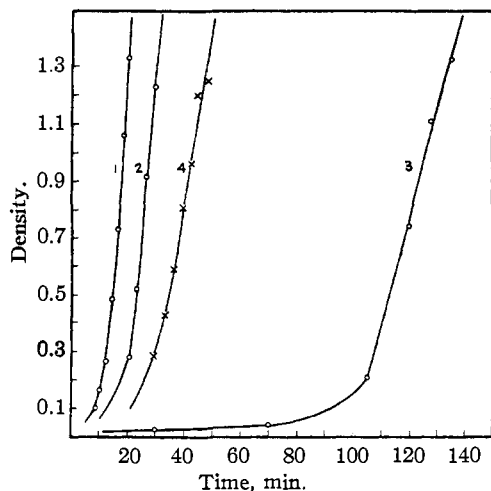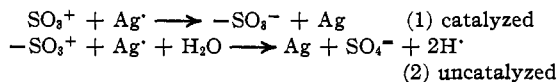
(9) S. E. Sheppard, *Phot. J.*, **59**, 135 (1919).

Fig. 1.—Reduction of Ag^+ by SO_3^-, variation of rate with sulfite concentration: Curve 1, 0.1 mmol. $AgNO_3$, 0.5 mmol. Na_2SO_3; Curve 2, 1.0 mmol. Na_2SO_3; Curve 3, 4.0 mmol. Na_2SO_3; Curve 4, 0.2 mmol. $AgNO_3$, 4.0 mmol. Na_2SO_3; temperature, 59.8°; total vol., 40 ml.

ciation constant of the silver sulfite complex of 4×10^{-8} at 60°. This value of the constant was obtained by extrapolation of unpublished data on the solubility of silver bromide in sodium sulfite over the temperature range 15–30°. The constant employed, therefore, is probably correct only as to order of magnitude, but this is sufficient for the present purposes.

TABLE I

REDUCTION OF SILVER IONS BY SODIUM SULFITE

Temp., 59.8°; reaction volume, 40.0 ml.

$AgNO_3$, mmol.	Na_2SO_3, mmol.	Excess SO_3^-	R^*	t^*, min.	$[Ag.]$ $\times 10^{-8}$	R^*/SO_3^-
0.10	4.0	3.8	0.044	105	1.1	0.0116
.10	1.0	0.8	.116	19	25.0	.145
.10	0.5	0.3	.164	11	180.0	.55
.20	4.0	3.6	.069	27	2.5	.019

The acceleration of the reaction rate in the early stages of the silver-catalyzed reaction is greater than is to be expected from a simple growth of the silver particles with proportionality between reaction rate and silver surface.[2,4,5] If the added silver nuclei are allowed to "grow" by partial reduction of the silver sulfite solution by hydroxylamine, subsequent reduction by the sulfite attains a considerably smaller rate than otherwise (cf. Curves 4 and 1, Fig. 2). These facts could be explained if the reduction by sulfite gives rise to new silver nuclei, in which case the total silver surface will increase at a greater rate. A possible mechanism for the reduction of silver ions by sulfite is the following

$$SO_3^+ + Ag^· \longrightarrow -SO_3^- + Ag \quad \text{(1) catalyzed}$$
$$-SO_3^+ + Ag^· + H_2O \longrightarrow Ag + SO_4^- + 2H^· \quad \text{(2) uncatalyzed}$$

Reaction (2) between the monothionate radical and the silver ion should occur with little or no energy of activation and, occurring homogeneously, could give rise to new silver nuclei. Thus, a special type of chain reaction may arise.

In keeping with this mechanism is the fact that very small amounts of copper sulfate catalyze the reduction of silver ions by sulfite, both in the presence and in the absence of added silver catalyst. This is illustrated in Fig. 2, and may be explained by the reaction:
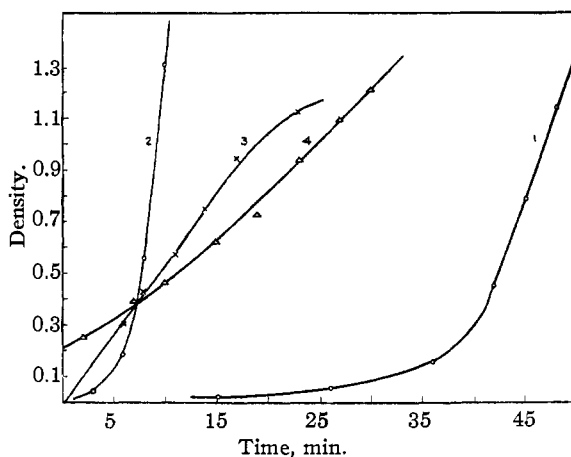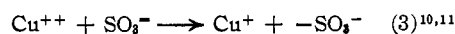
$$Cu^{++} + SO_3^- \longrightarrow Cu^+ + -SO_3^- \quad (3)^{[10,11]}$$

Fig. 2.—Reduction of Ag^+ by SO_3^-: Curve 1, colloidal silver added; Curve 2, colloidal silver plus 0.0001 mmol. copper sulfate added; Curve 3, 0.01 mmol. copper sulfate, no colloidal silver added; Curve 4, first 10% reduction by hydroxylamine, colloidal silver added; $AgNO_3$, 0.1 mmol.; temperature, 59.8°.

Sodium Stannite.—The silver sulfite complex (dissociation constant about 3×10^{-9} at 25°)[12] could not be used in a study of the reduction of silver salts by stannite ion, since reaction was too rapid. The thiosulfate complex ($K = 4.2 \times 10^{-14}$ at 25°)[12] gave a reaction time of several minutes. The stannite solution employed was prepared by dissolving 0.5 mmol. stannous chloride in 5.0 ml. N sodium hydroxide. A total volume of 40 ml. containing 0.10 mmol. silver nitrate and 2.0 ml. of 5% gum arabic was employed, and all operations were carried out under an atmosphere of oxygen-free nitrogen.

(10) Baubigny, Compt. rend., 154, 701 (1912); Ann. chim., 1, 201 (1914).

(11) J. Franck and F. Haber, Sitzber. preuss. Akad. Wiss., 250 (1931).

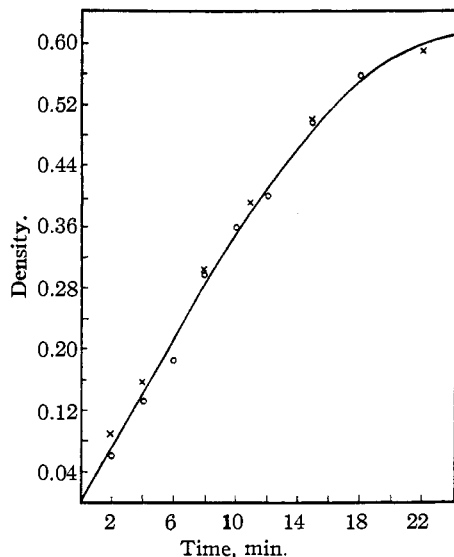(12) M. Randall and J. O. Halford, THIS JOURNAL, 52, 178 (1930).

Fig. 3.—Reduction by stannite: 0.10 mmol. AgNO₃ in 40 ml. 0.25 M Na₂S₂O₃; temperature, 20.0°; -O--O- no colloidal silver; -×---×- 1.0 ml. of Carey Lea silver sol added.

The reaction was somewhat erratic, but no evidence of silver catalysis could be detected. Typical data are given in Fig. 3. The measured rates indicate little dependence upon the thiosulfate-ion concentration, as shown by the data in Table II.

TABLE II

EFFECT OF THIOSULFATE CONCENTRATION ON REDUCTION OF THE SILVER COMPLEX BY STANNITE

Na₂S₂O₃ concn.	0.02	0.05	0.25	0.50	1.00
K^a............	0.048	0.048	0.048	0.051	0.067
		.071			

^{a} 1st order constant.   Time in minutes.

This indicates that the undissociated complex, rather than free silver ions, is attacked by the stannite.

Stannite reduction of the silver complex formed by dissolving silver iodide in excess potassium iodide occurs at a conveniently measurable rate. This reaction is definitely catalyzed by colloidal silver, and the reaction curve of the catalyzed reaction is of the same general form as that previously obtained for the reduction of silver ion by hydroquinone or hydroxylamine. In these experiments, a solution was prepared from 10 ml. of 0.01 M silver nitrate and 10 ml. of 2.0 M potassium iodide; 2.0 ml. of 5% gum arabic was added, and the stannite solution employed was the same as before. The total solution volume was 36 ml. Typical reaction curves for the presence and ab-
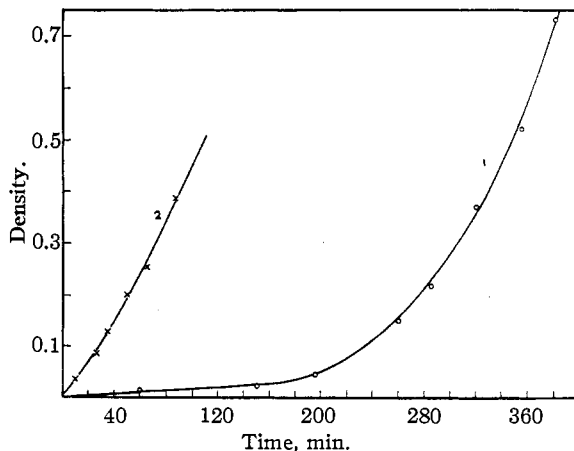

Fig. 4.—Reduction by stannite: 0.10 mmol. AgNO₃ in 36 ml. 0.55 M KI; temp., 29.8°; Curve 1, no colloidal silver added; Curve 2, 1.0 ml. of Carey Lea silver sol added.

sence of added colloidal silver are given in Fig. 4. The dependence of reaction rate upon temperature is given in Table III, where the reaction rates are determined as previously described for the hydroxylamine reaction.[4]

TABLE III

DEPENDENCE OF REACTION RATE ON TEMPERATURE

Temp., °C.	R	Temp. coeff.	Temp., °C.	t (D = 0.027) Min.	Temp. coeff.
20.0	0.0028		29.8	175	
29.8	.0056	2.03	39.8	38	4.6
39.8	.0111	1.98	49.8	10	3.8

Although the temperature coefficient of the uncatalyzed reaction can be but roughly inferred from the length of the "induction period" in the unnucleated reaction system, it is clear that this coefficient is considerably greater than that of the silver-catalyzed reaction.

Desylamine and Furoin.—Desylamine and furoin are of special interest to the present discussion. These compounds are not developers for the usual silver bromide emulsions, such as the motion picture positive or negative material. Under special working conditions, and with a heavily exposed unconventional type of emulsion, e. g., the Azo printing paper, a brown image of fair quality may be obtained by use of these agents. Normally, however, they reduce without selective action.

The reduction of silver ions from sodium sulfite solution was studied, using the standard procedure for reaction in the absence of oxygen. Because of the low solubilities in pure water, 16.7% eth-

anol solution was employed in the work with de-sylamine and 40% in the work with furoin. No silver catalysis was observed, and the reaction followed closely the first-order equation with respect to the reducing agent. The reaction rate, at least to a first approximation, was independent of the concentration of the silver ion or the silver sulfite complex, and was approximately equal to the rate of oxygen oxidation. The data for desyl-amine are given in Table IV. The reaction rates are expressed as first-order constants in terms of minutes.

TABLE IV

OXIDATION OF DESYLAMINE

Desylamine hydrochloride, 0.2 mmol.; 0.1 M borax, 10.0 ml.; 1.00 M NaOH, 1.10 ml.; total vol., 60 ml. 16.7% ethanol; temp., 20°C.

AgNO₃ mmol.	Na₂SO₃ mmol.	K/2.3	Remarks
0.10	0.50	0.00094	Nuclear sol added
0.10	0.50	.00098	No nuclear sol
1.00	5.00	.00101	No nuclear sol
0.10	5.00	.00090	No nuclear sol
Oxygen oxidation		.00087	

Furoin, 0.20 mmol., dissolved in 50 ml. of 40% ethanol buffered by 5.0 ml. of 0.1 M borax, gave a silver-ion rate of 0.00188, as compared with an oxygen rate of 0.00190.

From these results it appears that the rate-controlling process in the oxidation of desylamine and furoin by silver ion is the enolization of the reducing agent, just as in the case of the oxygen oxidation of desylamine,[13] and of the members of the benzoin series.[14]

Discussion

Silver catalysis of the reduction of silver ions is not a sufficient condition for developer action, but it may be a necessary one. Sodium sulfite, which certainly is not a developer, exhibits a strong silver catalysis in its reaction with silver ions. In this case, however, the reason why sulfite is not a developing agent is clear on kinetic grounds. At room temperature the reaction between silver ions and sulfite is so slow that it can be observed only after the passage of days. The sulfite, on the other hand, forms a soluble complex with silver ion, and it will in time dissolve the silver halide. The emulsion becomes "fixed out" before the reducing action has had a chance, or the sensitive layer has been so disrupted by the

solvent action of the sulfite that selective reduction is not in evidence.

Furoin and desylamine in solutions of the same compositions as those employed in the experiments already described develop a brownish image on heavily exposed Azo paper when used in the absence of oxygen. This developing action is not of the conventional type, and attempts to obtain development of a simple emulsion, such as normal motion picture positive, have failed completely. In the latter case, reduction occurs, but it is not selective. Furoin and desylamine, therefore, are examples of reducing agents which do not show silver catalysis and which, normally, are not developers. More experimental work is required before an adequate explanation of the specialized developing properties of furoin and desylamine can be given.

Sodium stannite is a very active reducing agent and reduces the silver thiosulfate complex and probably the sulfite complex without silver catalysis. It is interesting to note that, in the three cases studied, the rate of reduction by stannite parallels the dissociation constants of the complexes. In the case of the silver iodide complex a definite silver catalysis exists, but the reaction mechanism is not known. The necessarily great total salt concentration required by the iodide system and the small relative variation which it permits seriously handicap a kinetic study of the reaction.

A connection between the development process and the silver catalysis of the reduction of silver ions by developing agents appears from the following considerations: In both of the cases adequately studied, *i. e.*, hydroquinone[2] and hydroxylamine,[4] the catalytic action of the silver depends either wholly or in part upon adsorption of silver ions to the silver. The occurrence of such adsorption, deduced from the reaction kinetics, is supported directly by the work of Euler,[15] Proskurnin and Frumkin,[16] and Veselovsky.[17] Tartar and Turninsky[18] failed to detect adsorption of silver ions to powdered silver, but they did not specify what precautions were taken to keep the silver surface free from oxide coating, nor did they determine the extent of the surface employed.

(13) T. H. James and A. Weissberger, THIS JOURNAL, **59**, 2040 (1937).

(14) A. Weissberger, H. Mainz and E. Strasser, *Ber.*, **62**, 1942 (1929).

(15) H. v. Euler, *Z. Elektrochem.*, **28**, 446 (1922).

(16) M. Proskurnin and A. Frumkin, *Z. physik. Chem.*, **A155**, 29 (1931).

(17) V. I. Veselovsky, *Acta Physicochem. U. R. S. S.*, **11**, 815 (1939).

(18) H. V. Tartar and O. Turinsky, THIS JOURNAL, **54**, 580 (1932).

Oxide coating markedly decreases the adsorptive power of the silver.[17] Tartar and Turninsky attribute Euler's results to displacement of zinc impurity by silver, but this explanation could not account for the positive adsorption which Euler and Zimmerlund[19] found for the analogous case of silver ions on gold foil, nor for the results of the Russian investigators.

Erbacher[20] calculated from Euler's data that the saturation value of silver ions adsorbed to silver is around 2.8×10^{-6} millimole per square centimeter surface. This is in between the values for complete coverage by silver *atoms* (2.30×10^{-6}) and silver *ions* (3.73×10^{-6}). He concludes that the metal electron attracted by the adsorbed silver cation weakens the nuclear field of the adsorbed ion and thus increases the radius above that of the free ion. Similar deformation, modified by the crystal forces, is to be expected in the case of a silver bromide particle containing a silver nucleus, such as that produced by light action or partial reduction by a developing agent. This may be the basis for the enhanced reactivity toward certain reducing agents[21,22] which require an appreciable energy of activation. If, however, the activation energy of reaction between silver ions and a reducing agent is very small or zero, the deformation of silver ions at the silver surface could not increase the reaction rate significantly by virtue of a decrease in activation energy and, hence, no appreciable silver catalysis could arise from this cause. Reduction by stannite, furoin

and desylamine may be examples of the latter case.

Specific effects, such as adsorption of the developing agent to the silver halide or silver or both, may confer specific photographic properties upon a given developer. Further, reduction of silver ions from solution, either silver-catalyzed or homogeneous, will always compete to some extent with reduction at the interface. Such competition may be negligible, as is apparently the case in sulfite-free hydroquinone development.[23] It may also be serious if the developing agent forms a soluble complex with the silver ion,[8] or if the developing solution itself contains a strong silver halide solvent. Interesting photomicrographic evidence of such competition in the case of a *p*-phenylenediamine developer has been presented by Frieser.[24]

Summary

The rate of formation of metallic silver in a solution of the silver sulfite complex is markedly increased by the addition of colloidal silver or copper sulfate, and is dependent upon the silver-ion concentration. Sodium stannite reduces the silver thiosulfate complex without silver catalysis. A definite silver catalysis is observed in the reduction of the silver iodide complex ion by stannite. Desylamine and furoin reduce silver ion without silver catalysis and at rates approximately equaling those of the reactions with oxygen. The significance of these results for photographic development theory is discussed.

(19) H. v. Euler and G. Zimmerlund, *Arkiv. Kemi., Mineral Geol.,* **8,** No. 14 (1921).

(20) O. Erbacher, *Z. physik. Chem.,* **A182,** 243 (1938).

(21) S. E. Sheppard, *Phot. J.,* **69,** 330 (1929).

(22) G.-M. Schwab, H. S. Taylor and R. Spence, "Catalysis," D. Van Nostrand Co., New York, N. Y., 1937, p. 329.

(23) T. H. James, *J. Phys. Chem.,* **44,** 42 (1940).

(24) H. Frieser, *Atti X Congr. Int. Chim.,* **V,** 509 (1938); *Z. wiss. Phot.,* **37,** 240 (1938).