tates reaction. It may be observed further that the temperature coefficient of the $1/t$ rates varies considerably over the range employed, whereas the rates of continued reaction show a fairly constant temperature coefficient which is substantially smaller than that of the formation of the reaction centers.

In all of this, it is to be expected that reduction of silver ions can occur in solution, but, under the conditions employed, the direct attack upon the solid halide occurs at a substantially greater rate. If, however, the reaction in solution were sufficiently accelerated, it might successfully compete with the reaction at the surface. The addition of copper sulfate appears to accomplish just this. Copper sulfate catalyzes the reaction between silver ions in solution and hydroxylamine, giving rise to a large number of colloidal silver particles in solution which continue the catalysis.[7] In this case, gelatin can even cause an increase in the reaction rate under some conditions by stabilizing the colloidal silver.

Acknowledgment.—The author is indebted to Dr. G. Kornfeld for helpful criticism and discussion of this work.

Summary

1. Kinetic and microscopic studies have been made of the reduction by hydroxylamine of nucleated silver chloride precipitates.

2. Exposure to light of a pure silver chloride precipitate markedly increases the rate of reduction by hydroxylamine.

3. Reaction starts at discrete points on the halide surface. The number of active spots depends largely upon the previous history of the precipitate.

4. The temperature coefficient of the first stage of reaction between unexposed silver chloride and hydroxylamine is variable, but is larger than the coefficient of reduction of the nucleated precipitates.

5. Copper sulfate catalyzes the reduction of silver ions from solution, and its presence changes the character of the reaction between silver chloride and hydroxylamine.

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[7] T. H. James, THIS JOURNAL, **61**, 2379 (1939).

[COMMUNICATION NO. 761 FROM THE KODAK RESEARCH LABORATORIES]

Surface Conditions of Silver Halides and the Rate of Reaction. III. Reduction of Silver Chloride by Hydrazine

BY T. H. JAMES

Various investigators have suggested silver catalysis as a basis for the selective reduction of exposed silver halide by photographic developing agents. Volmer[1] suggested that silver catalyzes the oxidation of developing agents by silver halide, basing this suggestion upon the observation that colloidal silver accelerates the oxidation of these agents by air. Sheppard proposed a more specific catalytic action, namely, a catalysis of the decomposition (into silver and oxidized developing agent) of an adsorption complex formed between the agent and the silver halide. He showed that such a decomposition catalysis occurs in the case of the soluble silver sulfite complex ion.[2]

It has already been shown[3,4] that the reduction of silver ions from solution by hydroquinone, hydroxylamine, and *p*-phenylenediamine is catalyzed by colloidal silver. However, the reduction of silver chloride by hydroxylamine[5] and the reduction of exposed silver bromide by hydroquinone[6] do not appear to involve silver ions in solution, but rather the solid silver halide. In this connection, the case of hydrazine is of particular interest. The reduction of silver ions from solution by hydrazine is catalyzed by silver[7] and the catalysis appears to be just as marked as it is in the corresponding hydroxylamine reaction. Still, hydrazine is a very poor developing agent, reducing unexposed silver halide almost as readily as exposed, whereas hydroxylamine is as selective in its action as some of the best developing agents. It is therefore of interest to compare the reduction of silver chloride by hydrazine and by hydroxylamine.

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[1] M. Volmer, *Z. wiss. Phot.*, **20**, 189 (1921).

[2] S. E. Sheppard, *Phot. J.*, **59**, 135 (1919).

[3] S. E. Sheppard and C. E. K. Mees, "Investigations of the Theory of the Photographic Process," Longmans, Green and Co., London, 1907, p. 141.

[4] T. H. James, THIS JOURNAL, **61**, 648, 2379 (1939); *J. Phys. Chem.*, in press.

[5] T. H. James, THIS JOURNAL, **62**, 536 (1940).

[6] T. H. James, *J. Phys. Chem.*, **44**, 42 (1940).

[7] K. Jablczynski and S. Kobryner, *Roczniki Chemji*, **9**, 715 (1929).

The experimental procedure followed in the study of the hydrazine reactions is the same as that previously employed with hydroxylamine.[5] Hydrazine reacts with silver ion according to the equation

$$4Ag^+ + N_2H_4 \longrightarrow 4Ag + N_2 + 4H^+$$

and the reaction can be followed conveniently by measuring the evolution of nitrogen. In the following procedure, reaction was carried out at 20° unless otherwise specified, and in a solution buffered at *p*H 9.1 by means of borax. A 42% solution of hydrazine hydrate was employed for most of the work, and check runs employing a purified sample of hydrazine sulfate indicated that the hydrate solution contained no impurity which influenced the reaction rate. Figure 1 shows the effect of colloidal gold (curve 2), colloidal palladium (curve 3), and colloidal silver (curve 4) upon the rate of reduction by hydrazine of silver ions from a sodium sulfite solution. Gum arabic was added as stabilizer. Here, as in the case of hydroxylamine, the gold sol is much less effective than the silver as a catalyst.

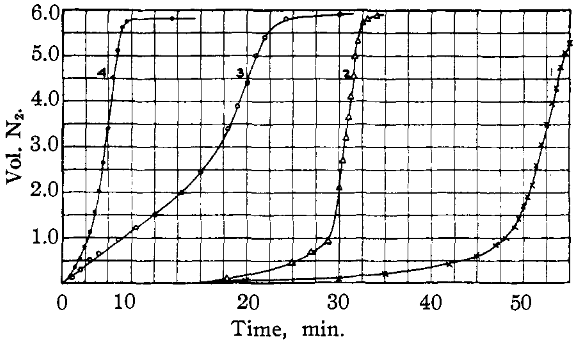

Fig. 1.—Reduction of silver ion by hydrazine: Curve 1, no added nuclei; Curve 2, colloidal gold added; Curve 3, colloidal palladium added; Curve 4, colloidal silver added.

The curves representing the reduction of silver chloride by hydrazine are less regular in form than those obtained with hydroxylamine, and the variation among duplicate runs is considerably greater. The silver obtained from the reaction is slate gray to black in color, in contrast to the silver gray metal obtained by hydroxylamine reduction. Exposure of the silver chloride precipitate to light under the conditions previously described[8] has little influence upon the course of the reaction, and nucleation by partial reduction with hydroxylamine decreases the induction period but does not eliminate it (see Fig. 2).

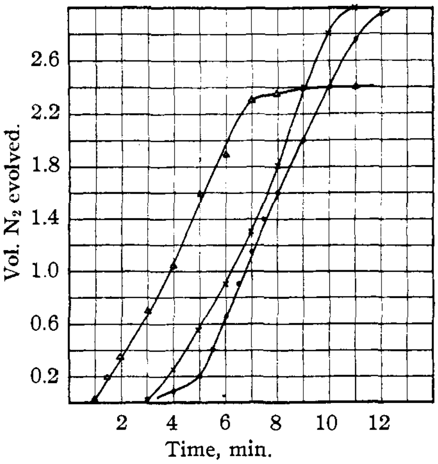

Fig. 2.—Reduction of silver chloride by hydrazine: —o—o—, pure AgCl; —×—×—, 5-min. exposure to light; —△—△—, nucleation by NH_2OH.

The effect upon the reaction course of the increase in hydrazine concentration is shown in Fig. 3. The extent of the induction period varies quite definitely with the hydrazine concentration, although it is somewhat less than a simple inverse proportion. The reaction rate beyond the induction period shows only a slight variation with hydrazine concentration.

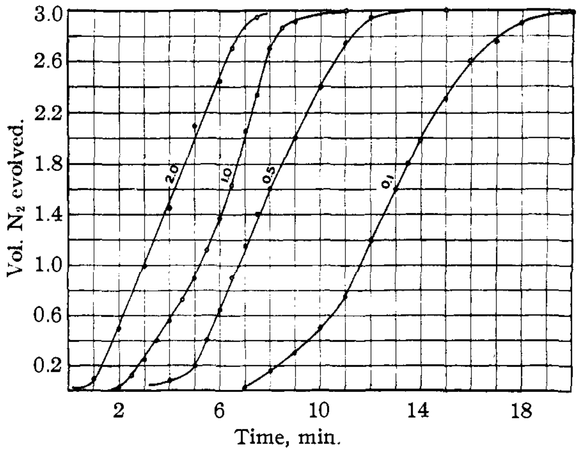

Fig. 3.—Hydrazine concentration series. Numbers on curves refer to milliliters of hydrazine solution.

The dependence of rate upon excess chloride-ion concentration is indicated by the data in Table I. The reaction rates are expressed in terms of the reciprocal of the time[9] required to complete 5% of the total reaction, the slope of the N_2-*t* curve at the point of 20% reaction, and the slope of the curve at the point of maximum rate.

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(8) T. H. James, THIS JOURNAL, **62**, 1649 (1940).

(9) The lower case "*t*" of this paper has the same meaning as "*T*" of Paper I, this series.

TABLE I

EFFECT OF EXCESS Cl^- UPON REACTION RATE: 1.00 ML. HYDRAZINE HYDRATE, 0.5 MMOLE AgCl

Excess Cl^- mmole/60 ml.	$1/t$ 5%	Slope 20%	Slope max.
0.5	0.40	0.32	0.70
2.5	.20	.136	.40
5.5	.102	.090	.23
10.5	.061	.054	.13

The effect of gelatin upon the reaction is shown in Fig. 4. The addition of 1.0 mg. of gelatin has only a small effect on the induction period of the hydrazine reduction, and further increases in gelatin produce significant increases in the induction period. This latter behavior strongly suggests reduction of silver ions *from solution*, and Fig. 5 gives the corresponding data for the reduction of silver ions from a sodium sulfite solution.

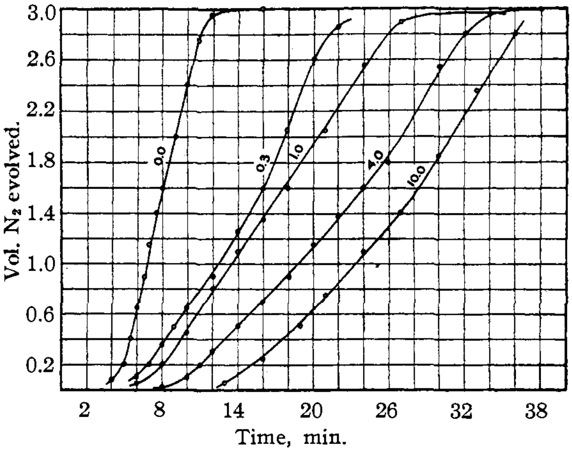

Fig. 4.—Effect of gelatin on reduction of silver chloride. Numbers on curves refer to milligrams of gelatin per 0.5 mmole of silver chloride.

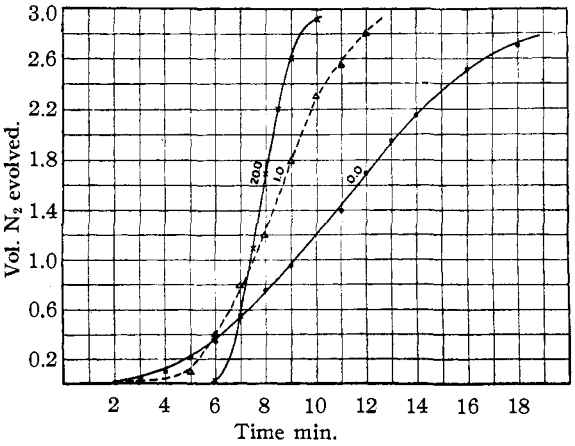

Fig. 5.—Reduction of silver ions from sodium sulfite solution; effect of gelatin. Numbers refer to milligrams gelatin.

The action of the sensitizing dye IVa (3,3′-diethyl-9-methylthiocarbocyanine chloride) is of interest (Fig. 6). When the surface of the silver chloride precipitate is half covered with the dye, the reaction course remains unchanged. When three-fourths of the surface is covered, there was some increase in the induction period, but no significant change in the course of the reaction beyond the induction period. When just the amount of dye required for complete coverage of the surface was added, the induction period was considerably increased, and the curve representing the continued reaction was changed in form. Addition of 2.5 times the amount of dye required to cover the surface resulted in a further increase in the induction period.

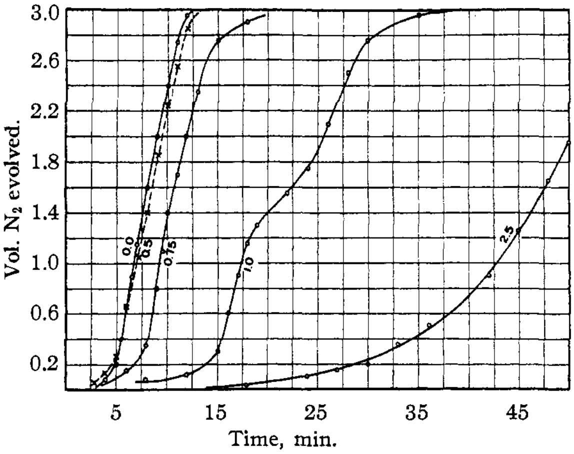

Fig. 6.—Effect of dye IV on reduction of silver chloride by hydrazine. Numbers on curves refer to dye added in terms of amount required to cover silver chloride surface.

The reduction of silver ions by hydrazine is very sensitive to the presence of small amounts of copper or copper salts. A silver nitrate–sodium sulfite–hydrazine solution which shows no sign of reduced silver after several minutes undergoes almost immediate reaction if merely stirred with a clean copper rod. Streamers of colloidal silver are observed passing out from the copper surface (with gum arabic added as stabilizer). Similarly, small amounts of copper sulfate added to the solution cause rapid reaction. Likewise, in the reduction of *silver chloride* by hydrazine, the addition of 0.005 mmole of copper sulfate to 60 ml. of the total solution volume reduces the induction period by four- or fivefold, and 0.05 mmole of copper sulfate eliminates it completely (Fig. 7). The silver remaining at the end of the reaction in the latter experiment has the appearance of platinum black.

The temperature coefficient of the reduction of silver chloride by hydrazine is about 2.8 over the temperature range 12–30°. The data are given in Table II.

TABLE II

TEMPERATURE COEFFICIENT OF REDUCTION OF AgCl BY N_2H_4

Temp., °C.	1/*t* (5%)	T.C.	Slope (20%)	T.C.
12.0	0.104	2.67	0.22	2.65
20.0	.23		.48	
29.8	.69	3.07	1.4	2.95

Discussion

In the reaction between silver chloride and hydrazine, it appears that reduction *from solution* predominates. The behavior of this reaction is in sharp contrast to the reduction of silver chloride by hydroxylamine in the absence of copper sulfate, but resembles the copper-catalyzed reaction. The differences in the absence of copper are most apparent in the data on the effect of gelatin and dye. The addition of increasing amounts of gelatin to the solution containing the silver chloride precipitate resulted in a continual increase in the length of the induction period of the reaction with hydrazine. Further, as the gelatin concentration in solution increased, more and more of the reduced silver appeared in colloidal form. Qualitatively, similar results were obtained when the silver was initially present in solution in the form of the soluble silver sulfite complex ion. In this case, the increase in the induction period due to gelatin was somewhat smaller, and the rate of the continued reaction showed an increase due presumably to stabilization of the colloidal silver formed (hence an increase in catalyst surface). The effect of the sensitizing dye IV on the reduction of silver chloride is quite small until the surface of the precipitate is almost completely covered. Larger amounts of dye result chiefly in an extension of the induction period, although some effect is apparent throughout the entire reaction. The same amounts of dye have no measurable effect upon the induction period in the reduction of silver ions from sodium sulfite solution.

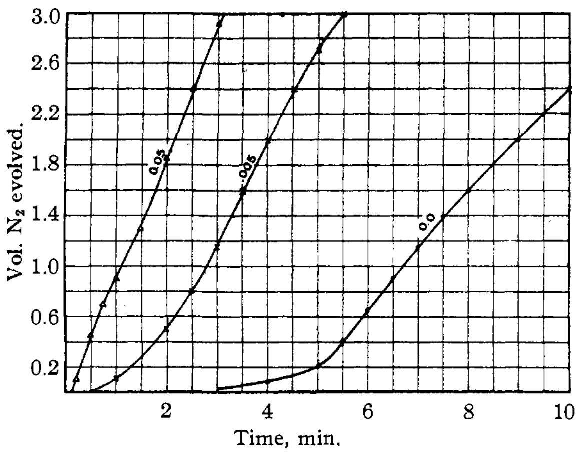

Fig. 7.—Effect of cupric sulfate on reduction of silver chloride. Numbers on curves refer to millimoles of cupric sulfate added per 60 ml. of solution.

The quantitative differences observed between the effects of gelatin and dye IV upon the reduction of silver chloride and the reduction of silver ions from sodium sulfite solution may be due to two or more factors. The rate of solution of silver chloride may play some part in the total effect. The results of Reinders and van Nieuwenburg[10] indicate that gelatin has no retarding action on the rate of solution of silver chloride by ammonia, but they did not allow adequate time for the formation of the adsorbed gelatin layer. Gelatin, once adsorbed, is tenaciously held by the silver halide[11] and it is not unreasonable to suppose that such a layer may have some effect. In the case of dye IV, the retarding action is clearly a surface effect, since the dye has no action on reduction from solution. The fact that the addition of dye in amounts exceeding the requirements of a monomolecular layer results in further increase in the induction period suggests that the excess dye acts to repair breaks in the original adsorbed layer occurring as a result of solution and reaction effects. This would be a kinetic process, and hence would depend upon the concentration of excess dye in solution. The formation of a secondary dye layer on the silver halide surface does not appear to take place with the dye excess employed in these experiments.[12]

A second source of difference between the reduction of silver chloride and of silver ions from the sulfite complex may arise from a tendency of the halide to act as a surface for deposition of silver from solution.[13] In the reduction of silver

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[10] W. Reinders and C. J. van Nieuwenburg, *Kolloid Z.*, **10**, 36 (1912).

[11] S. E. Sheppard, R. H. Lambert and R. L. Keenan, *J. Phys. Chem.*, **36**, 174 (1932).

[12] S. E. Sheppard, R. H. Lambert and R. D. Walker, *J. Chem. Physics*, **7**, 265 (1939).

[13] *Cf.* S. E. Sheppard and G. Meyer, THIS JOURNAL, **42**, 689 (1920); G. W. W. Stevens and R. G. W. Norrish, *Phot. J.*, **78**, 513 (1938).

ions from the sulfite complex, some silver plating on the walls of the reaction vessel invariably occurred, but very little or no plating was obtained in the reduction of silver chloride.

Further evidence favoring the predominance of reduction of silver ions from solution in the silver chloride–hydrazine reaction is found in the effect of excess chloride ion upon the reaction rate. If equilibrium conditions prevail, as they may in the absence of gelatin or dye adsorption, the silver-ion concentration will vary inversely as the excess chloride-ion concentration. In Fig. 8 the rates of reduction of silver chloride and silver ions from sulfite solution are compared with respect to dependence upon the equilibrium silver-ion concentration. The dissociation constant of the silver sulfite complex at 20° is not known, so the constants employed in both calculations were for 25°. Thus, the absolute values are in error, but the relative values and the orders of magnitude are correct. The results show that the relative dependence of the reaction rate upon the silver-ion concentration in solution is about the same in the two cases.

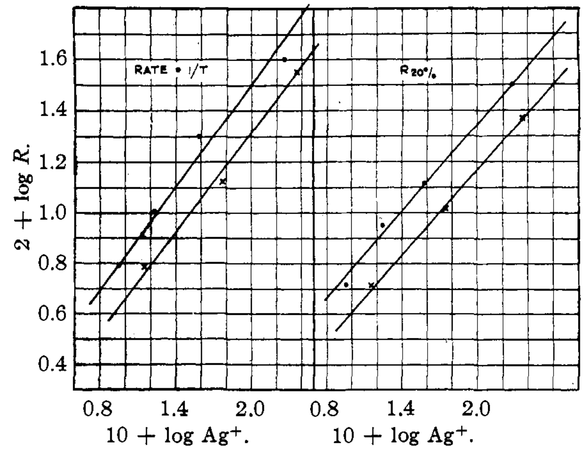

Fig. 8.—Comparison of reduction of silver chloride and $Ag(SO_3)_2^=$ by hydrazine, variation with silver ions: —○—○—, AgCl; —×—×—, $AgNO_3$-Na_2SO_3.

The fundamental reason for the difference between the action of hydroxylamine and hydrazine in the reduction of silver chloride is not clear, but it may be associated with the greater solvent action of the latter. Hydrazine might be expected to act in this respect much like ammonia. Hydrazine forms complexes with the silver halides[14] which are similar to the ammonia complex salts, except that the former are much less stable and readily decompose into silver and nitrogen. Although the existence in solution of a hydrazine complex ion similar to the ammonia ion $Ag(NH_3)_2^+$ has not been established, it is quite possible that such an ion has a temporary existence in solution and is an intermediate in the reduction of silver ions by hydrazine.

The important result from the point of view of development theory is that the agent which reduces silver chloride by direct attack upon the solid halide is a good developing agent (hydroxylamine), whereas the agent which acts predominantly by reducing silver ions supplied to the solution by the silver chloride is a very poor developing agent (hydrazine), even though both reactions show a pronounced silver catalysis.

Acknowledgment.—The author is indebted to Dr. G. Kornfeld for helpful criticism and discussion of this work.

Summary

1. Kinetic studies have been made of the reduction by hydrazine of precipitated silver chloride and of silver ions from sodium sulfite solution. The results are compared with the corresponding reductions by hydroxylamine.

2. The evidence indicates that the reduction of silver chloride by hydrazine is dependent upon the reduction of silver ions from the solution.

3. The significance for photographic development theory of the results obtained is discussed.

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[14] H. Gall and H. Roth, *Z. anorg. Chem.*, **214**, 201 (1933).