

sulfanilamide or one-tenth of that of sulfanilamide. For the corresponding  $N^4$ -arylidine derivatives the values are decidedly higher.<sup>5</sup> Thus, on the basis of these few compounds, indications are that the activity of not only the  $N^1$ -substituted sulfanilamides is lowered by introduction of the benzyl group, but also that, in comparison to the  $N^4$ -arylidine- $N^1$ -substituted sulfanilamides, activity is considerably diminished. This evidence suggests the possibility that the activity of the arylidene derivatives may be due to an *in vivo* rupture of the unstable anil linkage, with subsequent liberation of the active sulfanilamide moiety. Of the  $N^4$ -arylidene derivatives, recorded in Table II, whose relative antistreptococcal activity has been determined,<sup>8</sup> compounds 4, 9 and 10 were found to be equivalent to sulfanilamide, while compound 5 possessed a relative activity of about 86%.

#### Experimental

$N^4$  - (4 - Methoxybenzyl) -  $N^1$  - phenylsulfanilamide.—Three and sixty-six hundredths grams (0.01 mole) of  $N^4$ -(4-methoxy)-benzylidene- $N^1$ -phenylsulfanilamide<sup>6</sup> was dissolved in 100 cc. of dioxane (Eastman Kodak Co. "Histological"), 5.8 g. of Raney nickel<sup>9</sup> added, and the mixture hydrogenated at approximately three atmospheres of hydrogen. The mixture was filtered, concentrated to about 40 cc., and diluted with 100 cc. of water. The white precipitate was collected, washed with water and air-dried; yield 3.7 g., m. p. 154–55° (uncor.). Repeated crystallization from dilute alcohol gave a pure white product melting at 162–162.4° (uncor.).

$N^4$  - Acetyl -  $N^1$  - [4 - (benzyl) - amino] - phenylsulfanilamide.—Three and ninety-five hundredths grams (0.01

mole) of  $N^4$ -acetyl- $N^1$ -[4-(benzylidene)-amino]-phenylsulfanilamide was dissolved in 100 cc. of warm dioxane (Eastman Kodak Co. "Histological"), a small amount (about 2 g.) of Raney nickel<sup>9</sup> added and the mixture hydrogenated at 47–56° and approximately three atmospheres of hydrogen. The reaction mixture was filtered, concentrated to about one-half its volume and diluted with 200 cc. of water. The precipitate was collected, washed with water and air-dried; yield 2.7 g. After several crystallizations from dilute alcohol, white needles melting at 182–82.5° (uncor.) were obtained.

$N^1$  - [4 - (Benzyl) - amino] - phenylsulfanilamide.—Five and five-tenths grams (0.0139 mole) of  $N^4$ -acetyl- $N^1$ -[4-(benzyl)-amino]-phenylsulfanilamide was gently refluxed for two hours with 50 cc. of 5% sodium hydroxide. The alkaline solution was cooled, diluted with a little water, and acidified to litmus with dilute acetic acid. After cooling, the white precipitate was collected, washed with water and dried in air; yield 5.1 g. Several crystallizations from 95% alcohol, using a little decolorizing charcoal, gave white needles, melting at 174–175° (uncor.).

#### Summary

A brief series of  $N^4$ -aryl- $N^1$ -substituted sulfanilamides and a heterogeneous group of  $N^4$ -arylidene- $N^1$ -substituted sulfanilamides are reported. Preliminary biologic tests on a limited number of the  $N^4$ -aryl derivatives indicate that their antistreptococcal activity is much lower than that of sulfanilamide and certain  $N^1$ -substituted sulfanilamides. Moreover, their activity is considerably inferior to that of the corresponding  $N^4$ -arylidene derivatives. Of the new  $N^4$ -arylidene compounds tested, several showed an antistreptococcal activity equivalent to sulfanilamide.

(9) Covert and Adkins, THIS JOURNAL, 54, 4116 (1932).

KALAMAZOO, MICHIGAN

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## Surface Conditions of Silver Halides and the Rate of Reaction. II. Reduction of Nucleated Silver Chloride

By T. H. JAMES

The reduction of precipitated silver chloride by hydroxylamine appears to result from the direct attack of the reducing agent upon the solid silver halide.<sup>1</sup> Reaction apparently starts at discrete points on the silver chloride surface and continues at the silver-silver chloride interface, but the auto-accelerating nature of the reaction curve made unsatisfactory any attempt at a detailed analysis of the data previously avail-

able. It was not certain whether the number of reaction centers depends solely upon the previous history of the precipitate or varies with the reaction conditions. In order to clear up this point, and to obtain a more detailed mechanism of reaction, kinetic and microscopic studies of the reduction of nucleated silver chloride precipitates have been made.

The materials and general procedure employed have already been outlined. Several procedures

(1) T. H. James, THIS JOURNAL, 62, 536 (1940).

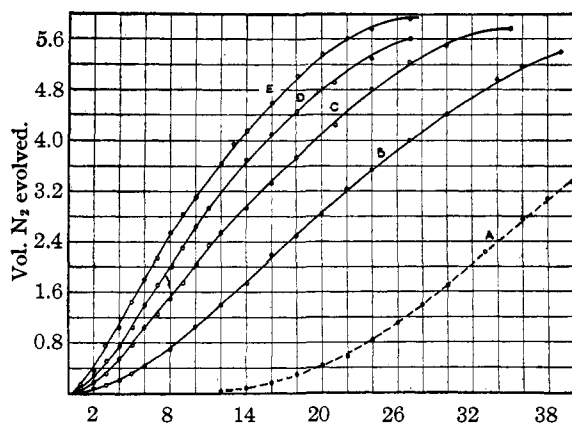


Fig. 1.—Effect of age of exposure on reduction of silver chloride by hydroxylamine: curve A, no exposure; curve B, exposure 17 hr. old; curve C, exposure 6 hr. old; curve D, exposure 2 hr. old; curve E, exposure 20 min. old.

were tried for introducing silver nuclei into the precipitates. The rate of reduction of a precipitate prepared in the presence of colloidal silver is markedly greater than that of a pure precipitate, but the use of colloidal silver introduces undesirable complications. Reliable results over a series of experiments could be obtained only when the silver sol employed was stabilized by a protective colloid. This, even though present in very small amounts, constitutes an undesirable impurity, and in addition results in an increase in the specific surface of the precipitate, as determined by dye adsorption. Two other methods of nucleation which avoid these undesirable features were finally adopted: exposure of the aged precipitate to light, and partial reduction of the precipitate by an amount of hydroxylamine insufficient to effect complete reduction. Since the oxidation products of hydroxylamine, under the conditions employed, are nitrogen and water, the latter procedure introduces no impurity. Nucleation was carried out at  $pH$  9.0 in the presence of 5.0 ml. of 0.1  $M$  borax at  $20^\circ$ . One-half millimole silver chloride was used in each experiment, and the precipitate was allowed to age eighteen hours before nucleation. Subsequent reactions were at  $pH$  7.18, where the solution was buffered by the addition of 10.0 ml. of 0.4  $M$  disodium phosphate. Unless otherwise specified, reduction was at  $20.0^\circ$ .

**Effect of Exposure.**—Exposures were made to white light supplied by a 60-watt tungsten lamp at 25 cm. During the exposure the precipitate was kept suspended in the supernatant liquid by

rapid mechanical stirring. From the volume of nitrogen evolved on subsequent reduction by hydroxylamine, it appears that the amount of reduction effected by the light exposure did not exceed 1% of the total silver chloride in any experiment.

The reaction rate decreases rather rapidly as time elapses between exposure and addition of hydroxylamine. This is illustrated in Fig. 1. The induction period, so marked in the reaction of the pure silver chloride, is eliminated to a large extent by the exposure to light, but becomes more and more prominent again as time elapses between exposure and addition of the reducing agent. A similar effect was observed by Ollendorff and Rhodius<sup>2</sup> in a study of development by elon of gelatin-free silver bromide layers. The rate of reduction increases with the duration of exposure. This increase is apparent throughout the entire course of reaction, but it is most pronounced in the early stages of the reaction. Thus, reduction of a heavily exposed precipitate goes nearly to completion before appreciable reduction of an unexposed precipitate occurs. This is evident from Fig. 2, in which the volumes of nitrogen evolved during various reaction times are plotted as a function of the amount of exposure,  $E$ , in seconds. In these experiments, the time elapsing

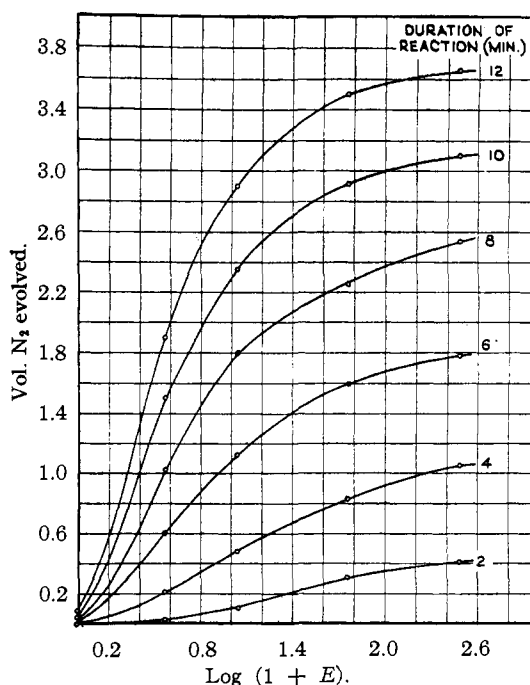


Fig. 2.—Effect of exposure on reduction of silver chloride.

(2) G. Ollendorff and R. Rhodius, *Z. wiss. Phot.*, **35**, 81 (1936).

between exposure and addition of hydroxylamine was held constant (twenty minutes).

**Nucleation by Hydroxylamine.**—In orienting experiments, the amount of hydroxylamine employed for nucleation was varied twenty-five fold, from the amount required to reduce 2% of the available silver chloride to that required to reduce 50%. Reduction was then continued under standard conditions, except that the amount of hydroxylamine now added was decreased by the amount used in the nucleation process. The reaction curves thus obtained could be superimposed upon the curve of the unnucleated precipitate by proper shift of the axes representing time and nitrogen volume. (The new axes,  $x + a$ ,  $y + b$ , were chosen so that the zero point of the curve representing the nucleated precipitate fell upon the curve representing the unnucleated precipitate at the point corresponding to the amount of reaction involved in the nucleation process.) This fact suggests that the state of a partially reduced silver chloride precipitate is the same, regardless of the amount of hydroxylamine used to bring about that degree of reduction, or whether the pH of the reducing solution was 9.0 or 7.18. In the subsequent kinetic experiments, the silver chloride was aged eighteen hours after preparation, then reduced 25 or 50% under controlled conditions before use.

Several of the partially reduced precipitates were examined by reflected light under a microscope (100X magnification). The color of the reduced silver was too much like that of the chloride for satisfactory direct observation, so the surface of the latter was "stained" with 3,3'-diethyl-9-methylthiocarbocyanine. Under magnification the surface of the 10% reduced precipitate appeared to consist of a number of silver spots of irregular shape surrounded by a field of violet-red (dyed silver chloride). The size of the silver spots increased with increasing reduction. Some fine particles of silver appeared well detached from the mass of precipitate, and probably resulted either from complete reduction of small crystals or from reduction of silver ions in solution. Observations on the dyed precipitates had to be made rather rapidly, since the halogen liberated during exposure to light rapidly decolorizes the dye.<sup>3</sup> The exact interpretation of the microscopic observations is doubtful, how-

(3) S. E. Sheppard, R. H. Lambert and R. D. Walker, *J. Chem. Physics*, **7**, 426 (1939).

ever, since the silver halide particles seen under the microscope are aggregates of tiny crystallites rather than individual crystals.

In the reaction rate experiments with the 50% reduced silver chloride precipitates, there was no induction period and the rate of evolution of nitrogen was almost constant for the first milliliter of gas. These rates in the subsequent tables are expressed in terms of milliliters of nitrogen per minute. The dependence of the rate upon the concentration of hydroxylamine is given in Table I. The reaction rate varies approximately as the 0.80 power of the hydroxylamine concentration.

TABLE I  
VARIATION OF REACTION RATE WITH  $\text{NH}_2\text{OH}$  CONCENTRATION

Concn. $\text{NH}_2\text{OH}$	pH	Reaction rate ml./min.
0.0156	7.18	0.097
.0312	7.19	.168
.0624	7.19	.275
.0940	7.18	.41

The variation of rate with chloride ion is given in Table II. From the constancy of the product,  $R \cdot (\text{Cl}^-)^{1.25}$ , given in the last column, it is evident that the reaction rate varies inversely as the 1.25 power of the concentration of excess chloride ion over the range studied.

TABLE II  
VARIATION OF RATE WITH EXCESS CHLORIDE-ION CONCN.

Excess $\text{Cl}^-$ mmoles/60 ml.	Reaction rate, ml./min.	$R \cdot (\text{Cl}^-)^{1.25}$
0.75	0.158	0.110
1.15	.092	.109
1.75	.056	.112
2.75	.0315	.111
4.75	.016	.112

Gelatin markedly decreases the reaction rate, and, as in the case of the pure precipitates, a minimum rate is obtained at quite low amounts of gelatin. In the present experiments with the partially reduced precipitates, the rate of reduction decreased rapidly during the evolution of the first 0.3 ml. nitrogen, then attained a value which remained almost constant during the evolution of the next 1.0 ml. The rates recorded in Table III are those obtained in the region of approximate constancy.

TABLE III  
EFFECT OF GELATIN ON REACTION RATE OF 50% REDUCED  $\text{AgCl}$

Gelatin, mg.	0.00	0.10	0.30	1.00	5.00
Rate	.158	.066	.020	0.015	0.016

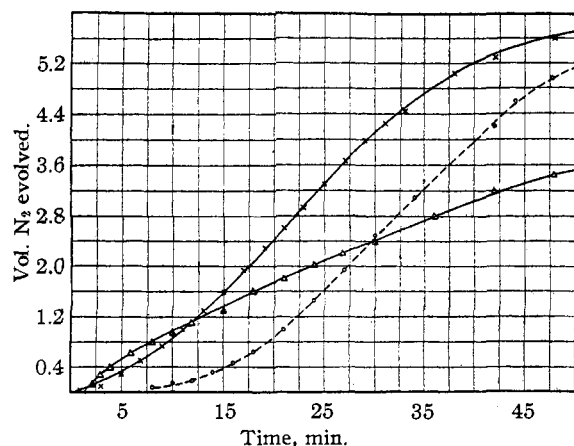


Fig. 3.—Effect of cupric sulfate on reduction of silver chloride by hydroxylamine: —○—○—, no addition; —×—×—, 0.005 mmole  $\text{CuSO}_4$ ; —△—△—, 0.05 mmole  $\text{CuSO}_4$ .

The sensitizing dye IVa (3,3'-diethyl-9-methylthiocarbocyanine chloride) reduces to a very low value the rate of reaction of the partially reduced precipitate. The reaction rates of the partially covered precipitates show a constant decrease as reaction proceeds.

TABLE IV

EFFECT OF DYE IV ON REACTION RATE OF PARTIALLY REDUCED (50%)  $\text{AgCl}$

Dye (ml. aqueous solution) <sup>a</sup>	Rate (initial), ml./min.
0.0	0.16
1.0	.14
2.0	.05
6.0	.0008

<sup>a</sup> Approximately 4.0 ml. of the solution saturates the surface of aged, unreduced  $\text{AgCl}$  precipitate.

**Temperature Data.**—The dependence of the reaction rate upon temperature was investigated for both pure and nucleated precipitates. In the case of the pure precipitates, the rates of reaction were determined as described in the preceding paper<sup>1</sup> (the rate of formation of reaction centers measured by the reciprocal of the time,  $t$ ,<sup>4</sup> required to effect 5% reduction; the rate of continuation process taken as the slope of the straight-line portion of  $V^{1/2} - t$  plot). Nucleation by light was effected by an exposure of five minutes fifteen seconds, and forty minutes elapsed between exposure and addition of hydroxylamine. During the last thirty-five minutes, the reaction vessel was placed in the thermostat to allow the solutions to come to temperature.

(4) This lower case " $t$ " has the same meaning as " $T$ " of the first paper of this series, ref. 1.

TABLE V  
TEMPERATURE COEFFICIENTS OF REACTION

Temp., °C.	1/ $t$	Pure precipitate		Nucleated precipitate				
		T.C.	R.	T.C.	25% R.	Red Light T.C.	Exposure R.	T.C.
12.00	0.022		0.0090	3.35	0.058	3.25	0.145	2.80
20.03	.073	4.46	.0237	3.15	.149	3.12	.332	2.87
29.80	.27	3.78	.073		.454		.925	

The recorded values are the averages of three determinations each. The variation among the triplicates ranged from a maximum of 3% in the case of the partially reduced precipitates to nearly 10% in the values representing the rate of formation of the reaction centers.

**Copper Catalysis.**—The reduction of silver ions by hydroxylamine in acid solution is catalyzed by copper sulfate. Accordingly, it was considered of interest to investigate the effect of copper sulfate on the reduction of unnucleated silver chloride. The effect of two concentrations of copper sulfate upon the course of the reaction is shown in Fig. 3. The addition of 0.005 mmole of copper sulfate to the reaction mixture decreased the induction period, but did not greatly alter the rate of continued reduction. However, the silver obtained at the end of the reaction was somewhat darker in color, and appeared to consist of finer particles. It was found that 0.05 mmole of copper sulfate completely eliminated the induction period and markedly changed the course of continued reaction. The silver obtained at the end of the reaction was almost black in color, as compared with the silver gray color of the product obtained normally. The change in character of the reaction brought about by the copper sulfate was emphasized by the effect of additions of gelatin. The data in Table VI show the effect of various amounts of gelatin on the times required to complete 5% and 50%, respectively, of the total reduction.

TABLE VI

EFFECT OF GELATIN ON COPPER SULFATE CATALYZED REACTION; COPPER SULFATE, 0.050 MMOLE

Gelatin, mg.	$t$ (min.) 5%	$t$ (min.) 50%
0.0	3.2	39
1.0	4.3	28
5.0	6.2	35
20.0	7.5	43

The reaction rate in this case decreases with the amount of gelatin added in a manner suggestive of the effect of gelatin upon the reaction between silver ions and hydroxylamine in sodium sulfite solution.<sup>1</sup> The minimum rate in the early

part of the reaction, so sharply defined at about 0.5 mg. of gelatin in the absence of copper sulfate, is not obtained for any gelatin concentration tried in the presence of copper sulfate, and the addition of 5.0 mg. scarcely reduces the rate to one-half of the original value. Furthermore, in the presence of copper sulfate and the larger amounts of gelatin, considerable quantities of colloidal silver are obtained, whereas, in the absence of copper sulfate, only a trace of the silver appears in colloidal form.

### Discussion

When the results of the present investigation are compared with those reported in the preceding paper of this series,<sup>1</sup> it appears that the number of reaction centers formed in the early stages of reduction of a well-aged silver chloride precipitate is approximately independent of the hydroxylamine concentration and the excess chloride-ion concentration. Nucleation with small amounts of hydroxylamine produces the same results as nucleation with large amounts, as far as is revealed by reaction rate measurements. The rate of reduction of unnucleated precipitates varies initially with the first power of the hydroxylamine concentration, but soon the power drops to 0.8. The rate of reduction of the nucleated precipitates varies rather closely with the 0.80 power of the hydroxylamine concentration, and it appears probable that adsorption of the hydroxylamine is involved at this stage. When nucleation is carried out in the presence of a fixed concentration of excess chloride, further reduction occurs at a rate which is inversely proportional to the 1.25 power of the chloride-ion concentration over the experimental range. When unnucleated precipitates are employed, the reaction rate in the initial stage varies approximately as the reciprocal of the excess chloride-ion concentration, but soon the rate becomes approximately inversely proportional to the 1.25 power of the excess chloride-ion concentration.

The data already given<sup>1</sup> for the variation of the reaction rates with the amount of adsorbed dye IV (partially covered surface) show that the number of reaction centers is not significantly altered by the presence of the dye, which appears to be spread quite uniformly over the surface.<sup>5</sup> Both the  $1/t$  rates and the slopes of the  $V^{1/3} - t$  straight-line plots representing 25% of the reac-

tion course varied directly with the amount of surface unoccupied by dye molecules.

The available evidence, therefore, indicates that reaction starts at certain active spots already existing upon the silver chloride surface. These active spots may be the cracks and imperfections in the crystals. The number of such spots is controlled by the previous history of the precipitate, and not by the immediate reaction conditions. The form of the reaction curve suggests that the number of reaction centers is relatively small in the absence of exposure to light or added colloidal silver. Beyond the first 3 to 5% of the reduction and up to 25 to 35%, the rate increases with the two-thirds power of the material already converted. It then remains approximately constant for a while, and finally decreases and approaches zero. The first stage corresponds to ever-increasing amounts of the silver-silver halide interface as the centers grow without merging boundaries. During the later stages, the centers are coalescing and the extent of the interface begins to decrease. When the precipitate has been exposed to light, however, the maximum rate is attained within the first 5% of the reaction course. In this case the nuclei may be much more numerous, and begin to coalesce quite early in the reaction.<sup>6</sup>

In the absence of exposure to light, the rate of formation of reaction centers on the silver halide surface is rather sensitive to reaction conditions. Under a given set of conditions, the reaction rates usually can be reproduced within 10% in duplicate runs, which is a considerably greater margin of error than that appearing in the rates of the continuation process. However, even a rapid shaking of the precipitate for thirty minutes before addition of the hydroxylamine was found to increase the  $1/t$  rate by about 25%, while the rate of continued reaction was substantially unchanged. Shaking the precipitate with silver obtained by complete reduction of silver chloride with hydroxylamine increased the  $1/t$  value even more, although a substantial induction period still remained. The rate of continued reaction once more was unchanged. It seems probable that, if reaction starts at faults and imperfections on the crystal surface, subjecting the precipitate to the mechanical abuse just described results in further damage at these points and thus facili-

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

(6) Cf. G. M. Schwab, H. S. Taylor and R. Spence, "Catalysis," D. Van Nostrand Co., New York, N. Y., 1937, p. 326.

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.<sup>7</sup> In this case, gelatin can even cause an increase in the reaction rate under some conditions by stabilizing the colloidal silver.

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

**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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## 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<sup>1</sup> 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.<sup>2</sup>

It has already been shown<sup>3,4</sup> that the reduction

(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.

of silver ions from solution by hydroquinone, hydroxylamine, and *p*-phenylenediamine is catalyzed by colloidal silver. However, the reduction of silver chloride by hydroxylamine<sup>5</sup> and the reduction of exposed silver bromide by hydroquinone<sup>6</sup> 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<sup>7</sup> 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.

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

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

(7) K. Jablczyński and S. Kobryner, *Roczniki Chemji*, **9**, 715 (1929).