3.—As higher molecular weight compounds are electrolyzed the main reaction seems to be one of coupling.

Certain generalizations can be made regarding structures necessary for nearly complete coupling.

A.—Straight chain free radicals of four carbon atoms or more will have approximately a 100% tendency to couple.

B.—Substituted *n*-propyl free radicals will have nearly a 100% tendency to couple.

It is interesting to consider the free radicals as substituted ethyl radicals, and it can be shown that there is a gradual increase in the tendency to couple as the ethyl radical becomes substituted with methyl groups. This is shown in Table II.

If we consider isopropyl and *t*-butyl as monomethyl and dimethyl substituted ethyl radicals, respectively, the effect of substitution on carbon number one is comparatively slight. If we consider *n*-propyl and isobutyl as mono-methyl and dimethyl substituted ethyl radicals, the effect on carbon number two is very marked. This analogy cannot be carried further, because, as has been stated, the higher molecular weight aliphatic radicals tend toward 100% coupling.

Summary

The products of electrolysis of the four butylmagnesium halides have been reported.

The products of the electrolysis of *n*-hexylmagnesium bromide in ethyl ether have been reported.

The relation between the structure of the free aliphatic radical liberated upon electrolysis and its tendency to couple has been presented.

Evanston, Ill. Received August 12, 1939

[Communication No. 752 from the Kodak Research Laboratories]

Surface Conditions of Silver Halides and Rate of Reaction. I. Rate of Reduction of Precipitated Silver Chloride

By T. H. James

The effects of adsorption during and subsequent to the preparation of silver halide precipitates and sols are clearly shown, in both the physical and in the chemical behavior of the resulting product. The very important role played by adsorption of sensitizing dyes and gelatin in the photochemistry of the silver halides has been demonstrated by the work of several investigators.[1] The effects of adsorption on the chemical reduction of silver halide are less well understood, and the problem is clouded by lack of concrete evidence on the mechanism of the reduction process. The fact that gelatin markedly retards the reduction of unexposed silver halide by developing agents has been known since the early days of the gelatin dry plate, but the manner in which the gelatin acts has been the subject of conflicting views. Reinders and van Nieuwenburg[2] found that the reduction of silver chloride by ferrous citrate was definitely retarded by as little as 0.0012% gelatin in the solution, and an increase in the gelatin concentration resulted in a further decrease in the reaction rate. They assumed that three steps were involved in the over-all process: (1) solution of the silver chloride, (2) reduction of the silver ions in solution; and (3) crystallization of the silver. They attributed the effect of gelatin to a retardation of the crystallization process. Sheppard, however, viewed the protective action of gelatin as an adsorption effect, and showed that a layer of gelatin of approximately molecular thickness is tenaciously held to silver bromide grains which have been prepared in the presence of gelatin.

A decision between the conflicting points of view evidently rests upon a knowledge of the mechanism of the reduction process. Hydroxylamine is a reducing agent well adapted to an experimental investigation of the problem. The reaction between hydroxylamine and silver ions has been studied.[3] Reduction of silver chloride proceeds with quantitative formation of nitrogen, and this allows a convenient method of following the reaction. In addition, hydroxylamine is a photographic developing agent and results ob-

---

[1] *Cf.* review of G. Kornfeld, *J. Phys. Chem.*, **42**, 795 (1938); also, S. E. Sheppard, R. H. Lambert and R. D. Walker, *J. Chem. Phys.*, **7**, 265, 426 (1939); S. E. Sheppard, R. H. Lambert and R. L. Keenan, *J. Phys. Chem.*, **36**, 174 (1932).

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

[3] T. H. James, This Journal, **61**, 2379 (1939).

tained with it should be directly applicable to the theory of the development process.

Materials and Procedure

Silver chloride was prepared by precipitation. Purified samples of silver nitrate and potassium chloride were employed in the preparation of the primary solutions. In the precipitation, 5.00 ml. of 0.20 *M* potassium chloride was added from a buret to a solution of 5.00 ml. of 0.10 *M* silver nitrate plus 10.00 ml. of water. The tip of the buret dipped beneath the surface of the silver nitrate solution, and stirring was maintained by a glass paddle rotated at the rate of 600 r. p. m. The time of delivery of the potassium chloride solution was twenty seconds. By this procedure, results reproducible within 5% could be obtained from day to day.

The reaction between the silver chloride and hydroxylamine was carried out in the apparatus previously described.[3] The silver chloride precipitates were, in general, allowed to age for eighteen to twenty-two hours before use, and when additions such as gelatin, dye, or excess chloride were made, sufficient time was allowed for equilibrium before addition of the hydroxylamine. The time required varied from a few minutes to several hours, depending upon the addition in question. The solutions were buffered at *p*H 7.25, and a total volume of 60.0 ml. was employed in the rate measurements. The temperature was 20.0 ± 0.03°. All operations were carried out in a photographic dark room. When sensitizing dyes were employed, a no. 3 Wratten safelight was used. For all other cases, a no. 1 safelight sufficed.

The specific surface of the silver chloride precipitates was determined by the amount of dye IVa (3,3′-diethyl-9-methylthiocarbocyanine chloride) adsorbed. The dye solution was added in slight excess, and, after equilibrium had been attained, the excess dye in solution was determined by comparison with a series of standards. The dye adsorption is irreversible.[4]

Experimental Results

The general form of the reaction curve is given in Fig. 1. The shape of the curve suggests a strongly autocatalytic reaction, and this is confirmed by the fact that the introduction of colloidal silver into the silver chloride precipitate at the time of preparation markedly increases the rate of reduction. The shape of the reaction curve of the un-nucleated silver chloride is similar to that obtained for the reduction of silver ions by hydroxylamine in the presence of gold nuclei,[3] and, just as in that case, a plot of the cube root of the nitrogen volume against the time yields a straight line over one-fourth to one-third of the reaction course. This is illustrated by curve 2 of Fig. 1. In general, the points representing volumes of less than 0.3 fell definitely away from the straight line, and the line cut the "*t*" axis at finite values. Accordingly, the time, *T*, at which a nitrogen volume of 0.30 was obtained (representing 5% of the reaction course) was taken as a representation of the rate of formation of silver nuclei. In the following, the rate itself is expressed as the reciprocal, $1/T$. However, the relative results do not vary appreciably if any other sufficiently small value of the nitrogen volume is chosen for the determination of the rate. A measure of the rate of the silver-catalyzed reaction is given by the slope of the straight-line plot, and the values obtained are included in the subsequent tables. However, we are concerned here chiefly with the rate of the preliminary reaction. Discussion of the silver-catalyzed reaction will be reserved for a later paper in which results of an investigation of nucleated silver chloride precipitates will be presented.

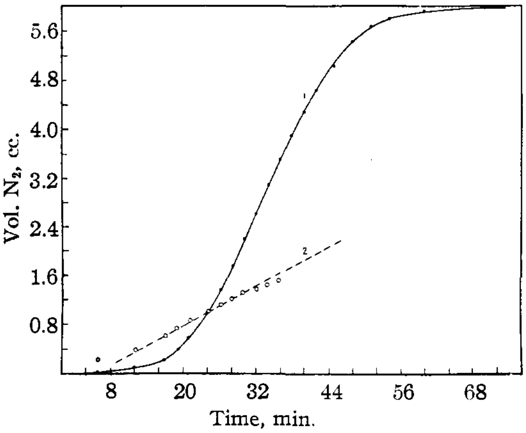

Fig. 1.—Reduction of AgCl by NH_2OH: Curve 1, V-t plot; Curve 2, $V^{1/3}$-t plot.

Effect of Age of the Precipitate on the Reaction Rate.—If a freshly prepared silver chloride precipitate is allowed to stand in contact with the mother liquor, the specific surface, as determined by dye adsorption, decreases at first and eventually attains a minimum value.[5] In the presence of excess chloride, the minimum is attained within a few hours. In the present investigation,

TABLE I

EFFECT OF AGE OF PRECIPITATE ON REACTION RATE

Age	*T*, min.	$1/T$	Slope
6 min.	2.4	0.415	0.142
12 min.	3.15	.317	.127
30 min.	4.05	.247	.127
95 min.	5.0	.200	.127
5 hr.	5.35	.187	.120
19 hr.	6.8	.147	.112

---

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

(5) I. M. Kolthoff and H. C. Yutzy, THIS JOURNAL, **59**, 1215 (1937).

the aging of the precipitate is very well represented by the change in the rate of the initial reaction with hydroxylamine. The rate data are given in Table I. In Fig. 2, the curve represents the specific surface in arbitrary units as a function of age, and the crosses represent the reaction rates. The agreement is almost too good.

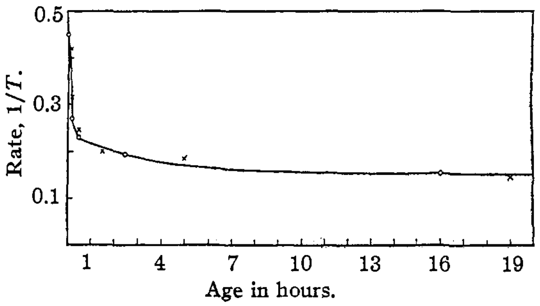

Fig. 2.—Effect of age of precipitate on rate of reaction: —O—O—, specific surface; × ×, reaction rate.

Variation of Rate with the Amount of Free Surface.—The well-aged silver chloride precipitate employed adsorbed 0.105 mg. of dye IVa at saturation, and the covered precipitate was attacked by hydroxylamine at a very low rate. An investigation was therefore carried out on a series of precipitates in which varying amounts of the surface were covered with the dye. The results are given in Table II. The calculated rates given in the last column are based upon the assumption that the rate of reaction is directly proportional to the available surface, and a small correction has been made for the finite "minimum" rate. The agreement between the experimental and calculated rates is quite good.

Table II

Variation of Rate with Available Surface

Fraction of surface covered by dye	T, min.	Slope	$1/T$	Calcd. rate
0	6.8	0.112	0.147	0.147
0.078	7.2	.110	.139	.136
.37	10.5	.082	.095	.095
.39	10.8	.078	.0925	.092
.50	13.2	.073	.076	.076
.50	14.0	.067	.071	.076
.75	25.0	.030	.040	.041
1.00	$\sim$200	..	$\sim$ .005	.005

Variation of Rate with the Amount of Gelatin.—The rate of the reaction decreases sharply as gelatin is added to the system, and attains a minimum value when the amount of gelatin employed is still quite small. This effect is shown in Fig. 3 and Table III.

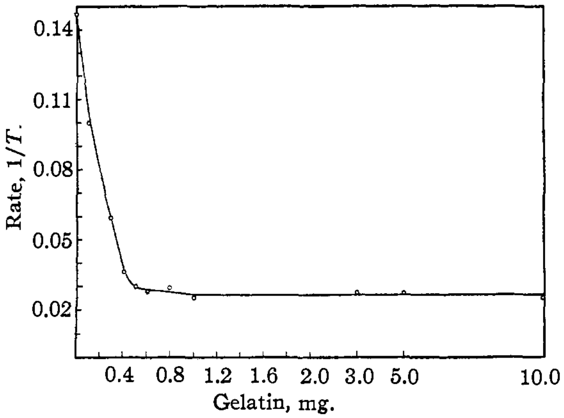

Fig. 3.—Variation of initial rate with amount of gelatin.

Table III

Variation of Rate with Amount of Gelatin

Gelatin: Eastman De-ashed Purified Product

Gelatin, mg.	T, min.	Slope	$1/T$
0	6.8	0.112	0.147
0.10	10.0	.058	.100
.30	16.9	.047	.059
.40	27.5	.047	.036
.50	33.5	.047	.030
.60	36.5	.043	.028
1.00	40	.038	.025
3.00	37	.043	.027
5.00	37	.038	.027
10.00	40	.038	.025

When a portion of the silver chloride surface was covered with dye IVa, the minimum reaction rate in the presence of gelatin was decreased by approximately the amount calculated on the basis of strict proportionality. The time required to attain equilibrium between the silver chloride and gelatin was increased, however. This is indicated by the data in Table IV. The time required for equilibrium in the absence of dye was, in general, not greater than one hour.

Table IV

Effect of Gelatin on the Reaction of Silver Chloride Partly Covered by Dye IVa

Fraction of surface covered by dye	Gelatin, mg./10	Time of agitation with gelatin	T, min.	$1/T$
0	0.50	2 hr.	37.0	0.027
0.33	.10	1 hr.	46.4	.0216
.33	.10	5 hr.	49.0	.0204
.33	.50	2 hr.	53.0	.0189
.33	.50	Calcd. for equil.		.0182

Gum arabic has a much smaller effect than gelatin. Moreover, no minimum rate was obtained in the experiments with gum arabic, as may be seen from an inspection of Table V.

TABLE V

EFFECT OF GUM ARABIC

Gum arabic mg.	T, min.	Slope	$1/T$
0	7.0	0.112	0.143
0.50	8.2	.079	.122
2.00	10.0	.076	.100
10.00	12.2	.073	.082
50.00	15.3	.060	.066

The rate of the initial reaction *varies directly with the hydroxylamine concentration.* This is evident from the constancy of the ratio, C/R, given in the last column of Table VI.

TABLE VI

VARIATION OF RATE WITH HYDROXYLAMINE CONCENTRATION

Hydroxylamine, mmole in 60 ml.	T, min.	Slope	$R = 1/T$	C/R
1.00	28.1	0.036	0.036	28.1
2.00	13.1	.067	.076	26.2
4.00	6.8	.112	.147	27.2

The rate varies *inversely as the excess chloride-ion concentration* under the experimental conditions employed. With the exception of the lowest concentration recorded in Table VII, the product $C{\cdot}R$ is reasonably constant.

TABLE VII

VARIATION OF RATE WITH EXCESS CHLORIDE ION

Added KCl in mmoles	Excess Cl^-, mmoles	T, min.	Slope	$1/T$	$C.R$
0	0.50	7.0	0.112	0.143	0.071
0.40	.90	17.0	.056	.059	.054
1.00	1.50	27.0	.038	.037	.0555
2.00	2.50	38.5	.016	.026	.052
3.00	3.50	66	.010	.105	.0525
5.00	5.50	110	.006	.009	.050

Discussion

The surface conditions of the silver chloride precipitate are of major importance in determining the rate of the initial stage of reduction by hydroxylamine. This is clearly shown by the close correlation between the specific surface and the reaction rate, both in the aging experiments and in the effect of an irreversibly adsorbed dye.

The effect of gelatin upon the reaction rate is of special interest. The curve representing rate as a function of the amount of gelatin breaks quite sharply, and additions of gelatin in excess of 0.5 mg. have little effect upon the reaction rate. The specific surface of the silver chloride, calculated from the adsorption of dye IVa (0.105 mg. per 0.50 mmole of AgCl) is approximately 9×10^2 sq. cm. The gelatin layer, therefore, exceeds molecular thickness.[6] Since gelatin in solution is not molecularly dispersed at the temperature employed in the present investigation (20°), it appears quite possible that the amount of gelatin required to produce the maximum effect upon the reaction rate will be smaller at higher temperatures. This point will be investigated later.

The failure of Reinders and Nieuwenburg[2] to obtain a minimum reaction rate at low gelatin concentrations might suggest a fundamental difference in the mechanism of the reaction which they studied. However, in their experiments, the gelatin was added to the reducing solution (Eder's ferrous citrate) preceding the addition of the silver chloride. Under these conditions, equilibrium between the gelatin and the silver chloride would not be obtained. Hence, rates of adsorption are involved in their experiments, and their results cannot be compared with those herein presented.

The form of the curve representing the effect of gelatin suggests that the gelatin is tenaciously held by the silver chloride and is probably irreversibly adsorbed. The decrease in reaction rate is to be attributed to this surface effect. These results do not support Reinders' suggestion that the effect is upon the rate of crystallization of silver from solution. In the present case, moreover, it is possible to measure the effect of gelatin on the reaction between hydroxylamine and silver ions in the presence of sodium sulfite,[3] and these measurements show a much smaller effect of gelatin than that encountered in the present work. The sharp minimum is not obtained. Thus, in one set of experiments in which silver ion was supplied by ionization of the silver sulfite complex, the rate, in the absence of gelatin, was 0.115. The addition of 1.0 mg. of gelatin reduced it to 0.071; of 5.0 mg. of gelatin to 0.051; and of 20 mg. of gelatin to 0.043.

The effect of gum arabic upon the reduction of silver chloride is much smaller than that of gelatin, and the form of the curve is different. The adsorption of gum arabic is probably reversible, and, in fact, the reaction rate data fit fairly well the expression derived from the Langmuir isotherm.

The adsorption of bromide ion[7] and iodide ion[8] by their respective silver salts does not follow the

---

[6] S. E. Sheppard, A. H. Nietz and R. L. Keenan, *Ind. Eng. Chem.*, **21**, 126 (1929).

[7] K. V. Astakhov and M. Suzdal'tzeva, *J. Phys. Chem. U. S. S. R.*, **6**, 1348 (1935).

[8] I. M. Kolthoff and J. J. Lingane, THIS JOURNAL, **58**, 1528 (1936).

Langmuir isotherm for small ion concentrations, and Kolthoff employs the equation

$$\Delta x = k \Delta \log a$$

for the adsorption of iodide ion to silver iodide. Such an expression obviously cannot hold for high ion concentrations where the surface is almost completely covered. Direct study of the adsorption in this region is beyond the power of ordinary analytical methods. It is of interest to note, therefore, that the reaction rate law suggested by the data in Table VII may be obtained directly from the Langmuir isotherm. The concentrations of chloride employed are such that the surface of the precipitate should be almost completely covered by the adsorbed monolayer, but the concentrations have not yet reached the values at which serious effects might be expected as the result of $AgCl_2^-$ formation.

The free surface, according to the Langmuir expression, is given by the equation

$$1 - \alpha = \frac{1}{1 + \beta c}$$

If c is relatively large, 1 may be neglected in comparison with βc, and the free surface will vary inversely as the chloride-ion concentration. Therefore, the rate, which varies as the free surface, varies inversely as the chloride-ion concentration.

The picture of the mechanism of the initial reaction suggested by the results of the present investigation is as follows. Hydroxylamine, in ionized form,[3] attacks those silver ions at the silver chloride surface which are not protected by adsorbed chloride ion or agents such as gelatin and adsorbed dye. It appears further that gelatin and possibly even the strongly held dye IV do not afford complete protection, but merely decrease the frequency of suitable contact between silver ions and hydroxylamine. Reduction of silver ions from solution may be definitely ruled out for the experimental conditions employed. At the end of the reaction, the silver is found in a white, spongy form which closely resembles the original chloride, whereas reduction of silver ions from solution yields silver powder or plating on the vessel walls. If reduction took place from solution, the effect of the gelatin and the dye could be explained only as an effect upon the rate at which the silver chloride dissolved. Solution, as the rate-controlling process, is not compatible with the catalytic action of silver and the direct proportionality between the rate and the hydroxylamine concentration.

Acknowledgment.—The author is indebted to R. H. Lambert and R. D. Walker of these Laboratories for information concerning the dye used in this investigation and for the calculation of the specific surface of the silver chloride precipitate.

Summary

1. The reduction of precipitated silver chloride by hydroxylamine has been studied with particular reference to the effects of aging of the precipitate, dye adsorption, gelatin adsorption and chloride-ion concentration upon the initial reaction rate.

2. The reaction rate closely parallels the change in specific surface with aging. The reaction is strongly inhibited by adsorption of the sensitizing dye, 3,3′-diethyl-9-methylthiocarbocyanine, to the silver chloride, and the reaction rate is approximately proportional to the free surface when the precipitate is only partly covered with the dye.

3. Gelatin markedly inhibits the reaction, and a minimum rate is obtained.

4. The kinetics of the process suggest that the initial reaction involves unprotected silver ions at the silver chloride surface. Under the conditions of this investigation, the silver ions do not pass into solution prior to reduction.

5. The effect of excess chloride-ion concentration upon the reaction rate suggests that, when the silver chloride surface is largely covered with chloride ions, further adsorption follows the Langmuir isotherm.

ROCHESTER, NEW YORK RECEIVED DECEMBER 8, 1939