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FORMATION OF THE SILVER HYDROSOL BY MEANS OF LIGHT

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I. Introduction

According to the study of S. Horiba and S. Chin[1], when a dilute solution of silver nitrate containing a small quantity of gelatin is illuminated, silver is reduced to yellowish- or reddish-brown colloid; however, if the gelatin sufficiently extracted with the electric conductivity water is used, no reaction occurs; but, if a trace of chlorine ion is added into the purified gelatin solution, a remarkable reaction is again brought about, that is, chlorine ion acts as a catalyser in this photochemical reduction of silver nitrate. The author investigated the reaction in more details.

II. Experimental

a) Materials

Merck's extra pure silver nitrate and extra pure sodium chloride, potassium bromide, and potassium iodide (pro analyse) were used. Gelatin solution used was obtained in the following way. Gelatin was first extracted by decantation with distilled water at intervals of 2, 4, and 12 hours, then twice with electric conductivity water at 12 hours intervals, and finally dissolved in the water bath at 40°C. By pipetting out 50 c.c. of this solution drying and weighing, the concentration of the gelatin solution was determined. The solution containing 0,032% gelatin thus made and 0.0004 mol silver nitrate was put in a non-alkaline beaker thoroughly washed by steam and it was exposed to intense direct sunlight, but the formation of hydrosol was by no means recognized.

b) Apparatus and experimental method

In Fig. 1, (E), the light source, was a 1500 watt tungsten filament incandescent lamp with a reflecting shade, being cooled incessantly by a motor fan. (L) was a convex lens 10 c.m. in diameter. In order to absorb heat radiation, (F) was filled with 5% copper sulphate solution 10 c.m. in thickness, which was covered with liquid paraffine to prevent the variation of concentration of the filter solution and clouding of the lens by the evaporation of water. The sides of (F)

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[1] S. Horiba and S. Chin, This Journal, 2, 49 (1928).

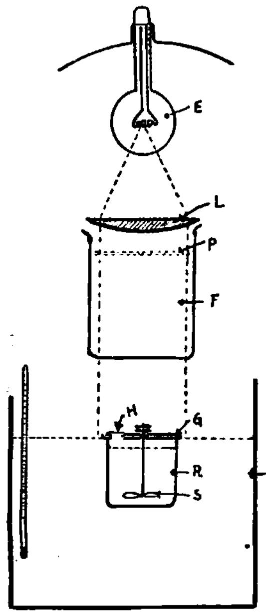

Fig. 1. Apparatus

were painted black to absorb diffused light. (R) was a reaction vessel, 7.5 c.m. in diameter, 300 c.c. in volume. Its upper section was covered with a disc made of plane glass (G). A hole 1 c.m. in diameter was made in (H), through which a small amount of the solution was taken out by a pipette. During the reaction the hole was covered with a microscopic cover glass. (S) was a stirrer made of non-alkaline glass. The reaction vessel was entirely put in the thermostat T. The temperature was 25°C., unless shown especially. By taking out 15 c.c. of the reacting solution the extinction coefficient of silver hydrosol was measured by means of the König-Martin's spectral photometer to observe the progress of the reaction. The extinction coefficient of the colloidal solution, ε, at a given wave length is expressed by

$$\varepsilon = \frac{\log \operatorname{tg} \alpha_1 - \log \operatorname{tg} \alpha_2}{d},$$

where α_1 is the angle of rotation of the ocular Nicol's prism in the case where both the fields of view of the prism are equal, when the absorption tube of the colloidal solution was set at the right and that of water at the left, and α_2 is the angle of rotation in the case when the absorption tubes were exchanged one with the other. d is the thickness of colloidal solution. An absorption tube 2 c.m. long was used. As the extinction coefficient is proportional to the concentration of the colloidal solution, the extinction coefficient obtained by observing α_1 and α_2 is taken as the measure of the concentration of the colloidal solution.

In order to examine whether or not Beer's law regarding light absorption can be applied to the photometer used for such a colloidal solution, the following preliminary test was carried out.

Table I.

Colour	Wave length Å (Hg)	Measure of drum	
Purple	3132 3126	29390 29790	29590
Blue	3341	38311 38565	38484
Green	3663 3655 3650	43681 44074	43878
Orange	5791 5770 5461	45891 46494	46192

The measure of the drum of photometer for a known wave length of the light source was observed by means of a mercury lamp, the results being shown in Table I. The extinction coefficients for lights of various wave length were measured for the

Table II.

Measure of drum	ε_1 Extinction coeff. after one hour exposure	ε_2 Extinction coeff. after two hours exposure	$\varepsilon_2/\varepsilon_1$
50000	0.01389	0.04799	3.45
46192	0.03363	0.12777	3.80
43878	0.05892	0.19206	3.26
38484	0.10871	0.28326	2.62

two cases where the reacting solutions were exposed to the sunlight for 1 hour and 2 hours, the values obtained being shown in Table II and Fig. 2. As to these two kinds of colloid, the ratios of the extinction coefficients may be regarded as much the same in the first three cases, that is, the state and property of the colloidal particles can be regarded as unchanged in such a range; the increase of the extinction coefficient is assumed to be caused only by the increase of number of the particles. The deviation of the fourth column from the other three is considered to be ascribed to the facts that the equal point of both fields of view of the ocular prism is hard to determine partly because of large extinction coefficient and partly because of the dark blue colour, and that there are some errors because the shorter the wave length is, the greater the effect of the colloidal particles on the reflection and diffusion of light is. From the above tests, green light was recognized to be best and, therefore, the drum of photometer was adjusted to the part 43878 and a 250 watt tungsten filament lamp used as the light source.

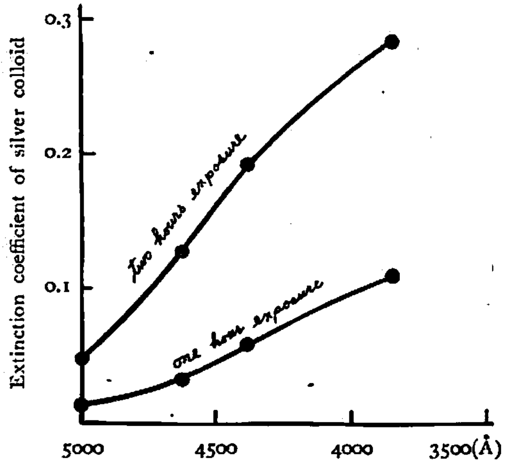

Fig. 2. Absorption curve of silver colloid.

Table III.

Relation between concentration and extinction coefficient

Relative conc. of colloid	Extinction coeff.	Extinction coeff./conc.
100	0.46870	0.47
80	0.37261	0.47
60	0.30640	0.51
40	0.21075	0.53
20	0.10001	0.50

Taking the relative concentration of silver hydrosol completely reacted by sufficient exposure to the sunlight as 100, the extinction coefficients were measured for respective colloidal solutions diluted at the ratio of 80, 60, 40, and 20. From the results shown in Table III and Fig. 3, it was ascertained that the relative concentration was almost proportional to the extinction coefficient.

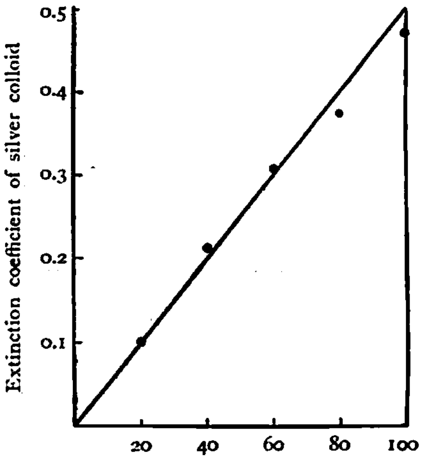

Fig. 3. Concentration and absorption

III. Experimental results

a) Relation between the concentration of chlorine ion and the reaction rate

250 c.c. of the solution containing 0.0004 N silver nitrate, 0.032% gelatin, and 0.000032 N sodium chloride were poured into a reaction vessel, 10 c.c. was taken out every 30 minutes and its extinction coefficient was measured by means of the König-Martin's spectral photometer. The results are shown in Table IV and Fig. 4. At the initial part of the reaction there exists a short induction period, but thereafter the extinction coefficient increases under zero order reaction. The measurements were repeated during three hours.

Table VI.

{ $AgNO_3$ 0.0004-N
{ Gelatin 0.032%

Conc. of NaCl	0.000032-N	0.000016-N	0.000008-N
time (min.)	Extinction coeff. of silver colloidal solution		
0	0.00784	0.00670	0.00000
30	0.03402	0.02604	0.00443
60	0.08415	0.06085	0.00505
90	0.18334	0.09976	0.01896
120	0.29002	0.15117	0.04684
150	0.38907	0.18788	0.06544
180	0.47716	0.22527	0.08919

With 0.000016 N and 0.000008 N, sodium chloride a series of observations were made in the same way, and in the both cases the curves of the similar type were obtained.

The appearance of the induction period is considered to be caused by the fact that it takes much time for reduced silver to grow up to such a particle size as capable of absorbing light. Another cause may be the auto-catalytic reaction by the silver nuclei as in the case of the reduction of silver halide by a reducing agent.

The reason why the pursuance of the reaction was stopped after three hours, is that the more highly concentrated solution darkened the field of view of the photometer and made the measurement difficult and, consequently, the result obtained was inaccurate. Moreover, the light of short wave length effective to the photo-chemical reaction was reflected, diffused, and absorbed by the colloidal particles formed, and so the light absorption by the reactant was not simple.

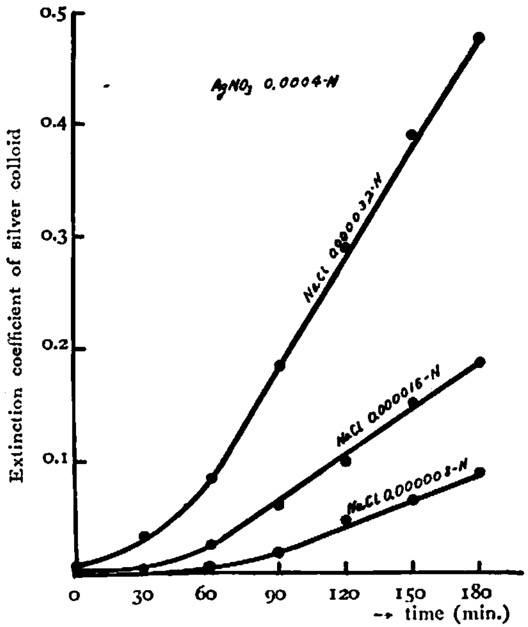

Fig. 4.

The effects of varying the concentrations of silver nitrate were observed by making the sodium chloride solutions of three different concentrations—0.000064 N, 0.000032 N, and 0.000016 N—react on 0.0002 N silver nitrate with 0.016% gelatin and on 0.0001 N silver nitrate with 0.008% gelatin. The results are shown in Tables V and VI, respectively.

b) Influences of halogen ions

When potassium bromide and potassium iodide were used instead of sodium

Table V.

$AgNO_3$ 0.0002-N
Gelatin 0.016%

Conc. of NaCl	0.000064-N	0.000032-N	0.000016-N
time (min.)	Extinction coeff. of silver colloidal solution		
0	0.00796	0.00165	0.00620
30	0.03841	0.00682	0.01340
60	0.11203	0.03465	0.01568
90	0.18972	0.06684	0.01972
120	0.25626	0.10876	0.03466
150	0.33300	0.14806	0.04545
180	0.39834	0.20289	0.06699

Table VI.

$\left\{\begin{array}{ll}\text{AgNO}_3 & 0.0001\text{-N} \\ \text{Gelatin} & 0.008\% \end{array}\right.$

Conc. of NaCl	0.000064-N	0.000032-N	0.000016-N
time (min.)	Extinction coeff. of silver colloidal solution		
0	0.00746	0.01846	0.01719
30	0.02546	0.02589	0.02188
60	0.06251	0.03770	0.02018
90	0.09708	0.05448	0.03238
120	0.15937	0.08572	0.04865
150	0.18323	0.09915	0.05885
180	0.21496	0.13996	0.06572

chloride, a reaction occurred slightly in the case of bromine ion and extremely slightly in the case of iodine ion, as shown in Table VII and Fig. 5.

Table VII.

$\left\{\begin{array}{ll}\text{AgNO}_3 & 0.0004\text{-N} \\ \text{Gelatin} & 0.032\% \end{array}\right.$

Conc. of halogen salts	NaCl 0.000040-N	KBr 0.000040-N	KI 0.000040-N
time (min.)	Extinction coeff. of silver colloidal solution		
0	0.00658	0.00961	0.00678
30	0.01150		
60	0.01884	0.02036	0.00981
90	0.03678		
120	0.05081	0.02630	0.01108
150	0.07571		
180	0.09102	0.03822	0.01047
240		0.04062	0.01123
300		0.04355	0.01589
360		0.05501	0.01503

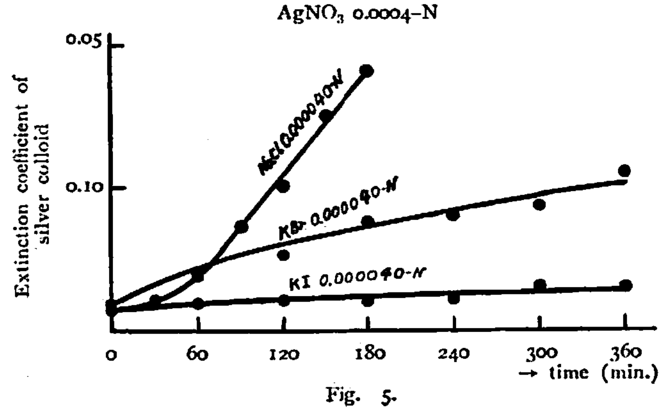

Fig. 5.

c) Monochromatic light

In all the above experiments white light from the lamp was used as it was. In order to measure the reaction rates in a monochromatic light, the following filter solutions were used. To obtain violet light, 0.005 g. crystal violet 2B and 15 g. copper sulphate were dissolved to 100 c.c. and this solution was used as a layer 2 c.m. in thickness. For yellow light, 6 g. of potassium chromate dissolved to 100 c.c. was used as a layer 7 c.m. in thickness. These solutions were used in (F) in Fig. 2. The experimental results are shown in Table VIII. In the case of chlorine ion a reaction occurred slightly, but, because of the weakening of light, the rate of its change was very small. In the case of bromine ion hardly any reaction occurred, and even iodine ion showed no reaction in yellow light.

Table VIII.

Effect of monochromatic light

$AgNO_3$ 0.0004-N
Gelatin 0.032%

Temperature 15°C	Purple		Yellow
Concentration of halogen salts	0.000040-N NaCl	0.000040-N KBr	0.000040-N KI
time (min.)	Extinction coeff. of silvercolloidal solution		
0	0.00693	0.00688	0.00839
60	0.01270	0.01346	0.00885
120	0.02272	0.01113	0.00794
180	0.03155	0.01561	——

d) Influence of gelatin

According to the experiments made by S. Horiba and S. Chin[2] there was hardly any influence found of the concentration of gelatin, which acted only as protective colloid. The present author made experiments on a solution only of silver nitrate and sodium chloride containing no gelatin. As shown in Table IX, the result was that though a little amount of dark grey precipitate was brought forth, no reaction proceeded.

Table IX

Effect of gelatin

$AgNO_3$ 0.0004-N
NaCl 0.000016-N
Gelatin nothing

time (min.)	Extinction coeff. of silver colloidal solution
0	0.01153
60	0.01464
120	0.01757
180	0.01478

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[2] S. Horiba and S. Chin, *loc. cit.*

e) Influence of oxalic acid

In the present reaction oxalic acid acts as a promoter. To a 0.0004 N silver nitrate solution, there was added a 0.00004 N sodium chloride solution containing 0.001 mol of oxalic acid at the rate of 2, 4, 8, 16, and 32 c.c., and after one hour the concentration change of each solution was measured. The results obtained are shown in Fig. 6 and Table X. The promoting action of oxalic acid is clearly recognized. It is considered that thoroughly extracted gelatin has lost the organic substances exerting such a promoting action by the extraction.

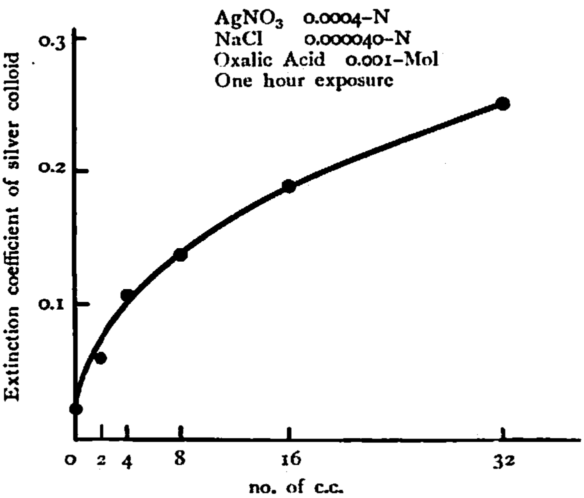

Fig. 6.

Table X.

Promoting action of oxalic acid

$AgNO_3$	0.0004-N
Gelatin	0.032%
NaCl	0.000040-N

Conc. of oxalic acid		Extinction coeff. of silver colloid	
No. of c.c.	mol/L	Initial	After one hour exposure
0	0.	0.00313	0.02154
2	0.000008	0.00344	0.05638
4	0.000016	0.00693	0.10756
8	0.000032	0.00298	0.13667
16	0.000064	0.00263	0.18861
32	0.000128	0.00541	0.24987

f) Effect of temperature

The temperature coefficient of the photographic dry plate is approximate to 1. With respect to the reaction of formation of silver hydrosol, a run of experiments were carried out with a solution of 0.0004 N silver nitrate and 0.000040 N sodium chloride at 15°, 25°, and 35°C., the results being shown in Table XI. The results show, though not so clearly, that the yield was maximum at 25°C. and decreased at 15° and 35°C.

Table XI.

Effect of temperature

$AgNO_3$	0.0004-N
NaCl	0.000040-N
Gelatin	0.032%

time (min.)	Extinction coeff. of silver colloidal solution		
	15°C	25°C	35°C
0	0.00713	0.00815	0.00753
60	0.02823	0.03369	0.03869
120	0.08337	0.11216	0.09720

IV. Considerations about the experimental results

a) In the present reaction, it is only silver chloride that absorbs the visible light, and it is, accordingly, inferred that the reaction starts from silver chloride. According to Plotnikoff[3], even $AgNO_3$ alone brings about a reaction by the action of light, if it is in the presence of an organic substance, according to the following formula:

$$AgNO_3 + H_2O \longrightarrow Ag + HNO_2 + O_2.$$

In the present experiment, however, a silver nitrate solution, to which was added the gelatin extracted with the electric conductivity water in order to remove the halogen ion perfectly, was illuminated with intense direct sunlight for a few hours. No change was recognized. This indicates clearly that even in the presence of an organic substance no reaction ensues by silver nitrate alone.

The progress of the reaction in the case of an extremely dilute solution was

Table XII.

Effect of solubility of silver chloride accompanied by temperature change

$AgNO_3$	0.0004-N
Gelatin	0.032%
NaCl	0.000004-N

time (min.)	NaCl 0.000004-N		NaCl 0.000002-N	
	Extinction coeff. of silver colloidal solution			
	15°C	35°C	15°C	35°C
0	0.01052	0.00622	0.00698	0.00556
60	0.01447	0.01128	0.00794	0.00799
120	0.04528	0.02658	0.01914	0.01254
180	0.08649	0.04354	0.03712	0.01894

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[3] J. Plotnikoff, *Allgemine Photochemie*, 2. Auflage, 459 (1936).

examined, taking account of the difference of the solubilities of silver chloride at 15° and 35°C., and it was found that the reaction rate v shows an increase directly proportional to the quantity of the solid silver chloride present, as shown in Tables XII and XIII.

Table XIII.

$\left\{\begin{array}{ll} AgNO_3 & 0.00040\text{-N} \\ \text{Gelatin} & 0.032\% \end{array}\right.$

Temp.	Cl^- conc. (mol/l. 10^6)	Dissolved AgCl (mol/L × 10^6)	Undissolved AgCl [AgCl] (mol/L × 10^6)	Reaction rate v ($\Delta\varepsilon$/min)	Reaction rate / undissolved AgCl $k=v/[AgCl]$ ($\Delta\varepsilon$/min. mol per L.)
15°C	4	0.187	3.8	0.00048	126.3
15°C	2	0.186	1.8	0.00021	116.6
35°C	4	1.03	2.9	0.00024	82.7
35°C	2	1.03	0.9	0.00011	122.2
					(mean) 111.95

The solid silver chloride, therefore, is activated by light absorption, and it is considered to start as follows:

$$AgCl + h\nu \longrightarrow AgCl'. \qquad (1)$$

From Table XI which shows the relation between the reaction rate and temperature, it is seen that the reaction rate is at its maximum at 25°C. and 35°C. It is easy to suppose that the reaction includes not only the photochemical decomposition of AgCl but also a thermal reaction. It follows that the decrease of the reaction rate at 15°C. may depend much more upon the decrease of the rate of thermal reaction than upon the increase of the photochemical reaction rate caused by the increase of undissolved silver chloride. The decrease of the reaction rate at 35°C. may be affected much more by the decrease of photochemical reaction rate caused by the dissolution of silver chloride than by the increase of the thermal reaction rate. Thus the reaction rate, on the whole, shows a decreased tendency and the yield is at its maximum at 25°C.

b) Gelatin used in the present reaction is considered to act not only as a protective colloid of the generated silver colloid, but as an acceptor of the chlorine atoms to be generated by the photochemical decomposition of silver chloride. As shown in Table IX, when no gelatin is contained, the reaction is almost perfectly retarded though some greyish-white precipitate is brought forth. This relation is respresented as follows:

$$AgCl + h\nu \rightleftarrows AgCl'. \qquad (1)$$

$$\mathrm{AgCl'+Gel.} \longrightarrow \mathrm{Cl-Gel.+Ag.} \tag{2}$$

Thus the reverse reaction of the primary photochemical reaction is retarded. In a solution the chlorine atoms thus generated easily turn into ions and, acting again on excessive Ag^+ ions, become solid silver chloride according to the following equation:

$$\mathrm{Ag^+ + Cl^-} \longrightarrow \mathrm{AgCl.}$$

This reaction is considered to be a kind of chain reaction carried by the chlorine ions.

c) The reactions of silver nitrate and sodium chloride at various concentrations, which have already been given in Table IV to VI, are summarized in Tables XIV and XV. When the concentration of silver ion is constant, the value of k (the ratio of the reaction rate v to the quantity of the undissolved silver chloride [AgCl]) is much the same, independent of the concentrations of the chlorine ion, e.g. 93.2, 38.9, and 24.8 for the concentrations of silver ion, 400, 200, 100×10^{-6} mol/L respectively. As in Table XIII, even in an extremely dilute solution in which the concentration of chlorine ion is $4 \sim 2 \times 10^{-6}$ mol/L, when the concentration of silver ion is 400×10^{-6} mol/L, the ratio, k, is 100 or so, being nearly equal to other values for silver ion in the same concentration.

Table XIV

Ag^+ conc. (mol/L·10^6)	Cl^- conc. (mol/L·10^6)	Dissolved AgCl (mol/L·10^6)	Undissolved AgCl [AgCl] (mol/L·10^6)	Reaction rate v ($\Delta\varepsilon$/min.)	Reaction rate / undissolved AgCl $k=v/[AgCl]$ ($\Delta\varepsilon$/min. mol per L)
400	32	0.46	31.5	0.003275	103.1
400	16	0.44	15.0	0.001349	86.5
400	8	0.43	7.6	0.000685	90.1
					(mean) 93.2
200	64	1.24	62.8	0.002333	37.1
200	32	1.00	31.0	0.001394	44.9
200	16	0.92	15.1	0.000525	34.8
					(mean) 38.9
100	64	4.69	59.3	0.001263	21.3
100	32	2.84	29.5	0.000760	25.7
100	16	2.01	13.9	0.000379	27.3
					(mean) 24.8

Table XV shows that when Cl^- is constant, k is nearly proportional to the

Table XV.

Cl^- conc. ($mol/L \cdot 10^6$)	Ag^+ conc. ($mol/L \cdot 10^6$)	Dissolved AgCl ($mol/L \cdot 10^6$)	Undissolved AgCl [AgCl] ($mol/L \cdot 10^6$)	Dissolved Ag^+ (Ag^+) ($mol/L \cdot 10^6$)	Reaction rate / [AgCl] $k=v/[AgCl]$ ($\triangle\varepsilon$/min mol per L)	$k/(Ag^+) \cdot 10^{-5}$)
32	400	0.46	31.5	368.5	103.1	2.81
32	200	1.00	31.0	169.0	44.9	2.66
32	100	2.84	29.5	71.5	25.7	3.46
16	400	0.44	15.6	384.4	86.5	2.25
16	200	0.92	15.1	185.9	34.8	1.87
16	100	2.10	13.9	86.1	27.3	3.17
64	200	1.24	62.8	137.2	37.1	2.70
64	100	4.69	59.3	40.7	21.3	5.23

concentration of the dissolved silver ion. The ratio of k to (Ag^+) is shown in the 7th column. However, the proportional constant is larger when the concentration of (Ag^+) is lower.

The photochemical reaction is initiated from the undissolved silver chloride. The particles of silver chloride, when forming colloid in the presence of an excess of Ag^+, form a kind of micelle which has adsorbed Ag^+ ions. The chlorine ions generated by the photochemical decomposition are considered to combine not with dissolved Ag^+ ions in the solution, but with Ag^+ ions on this adsorption layer and to be reduced to the original silver chloride. On the other hand, the Ag^+ ions on the adsorption layer, when consumed, must be supplied with the dissolved Ag^+ ions.

The rate of the recovery of this adsorbed Ag^+ ions depends upon the concentration of the dissolved Ag^+ ions in the solution, and upon the temperature of reaction. Therefore, this seems to be a cause of the fact that the reaction rate is apparently proportional to the dissolved Ag^+ ions. It is very difficult to give quantitative explanation to these relations. In the present experiment its reproducibility was found very difficult to obtain because of various conditions. Consequently, it is evident at least that this photochemical reaction is not a simple homogeneous reaction, but a heterogeneous system.

V. Summary

1) When a dilute solution of silver nitrate containing a little amount of gelatin is exposed to light, a stable and beautiful yellowish- or reddish-brown silver colloid is obtained.

2) In this reaction, halogen ion, particularly chlorine ion, exerts a remarka-

ble catalytic action and so the chain mechanism by chlorine ion has been proposed.

3) The reaction rate of formation of the silver colloid is proportional to the quantity of solid silver chloride, if the concentration of silver ion is constant, but at constant concentration of the chlorine ion it is proportional to the concentration of silver ion. These relations have been experimentally studied and discussed.

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