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#### Variation of Reaction Mechanism with Surface Conditions in the Reduction of Silver Salts by Hydroxylamine\*

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Silver bromide oxidizes hydroxylamine at pH 10.2-10.8 to nitrogen and water. Under comparable conditions, silver thiocyanate yields a mixture of nitrogen and nitrous oxide as the gaseous products. By varying the surface conditions of the thiocyanate, the composition of the reaction product may be varied over a wide range. Small additions of bromide or iodide greatly decrease the nitrous oxide yield. With initial partial coverage of the precipitate surface by gelatin, the nitrous oxide yield increases to a maximum. Further gelatin additions progressively decrease the yield. Aging a fresh precipitate increases the nitrous oxide yield. The results are explained by the effects of adsorption upon the relative rates of two competing reaction mechanisms.

#### INTRODUCTION

LTHOUGH the solubility product of silver thiocyanate lies close to that of silver bromide, the two salts behave quite differently in their reactions with hydroxylamine. For example, at pH 10.8 and in the presence of excess anion, silver bromide oxidizes hydroxylamine to nitrogen and water. Under the same general conditions, and at the same pAg, silver thiocyanate may yield 70-75 percent nitrous oxide and only 30-25 percent nitrogen. Variation in the surface conditions of the thiocyanate can markedly alter the nitrous oxide yield. Adsorbed gelatin and dye molecules strongly affect the composition of the gaseous reaction product. A thin coating of bromide or iodide suffices to decrease the nitrous oxide yield to only a few percent. These results have a definite bearing on the theory of photographic development.

#### EXPERIMENTAL

The experimental procedure followed closely that employed in previous investigations.<sup>1</sup> The specific surface of silver thiocyanate could not be determined by the simple titration with 3,3'-

TABLE I. Adsorption of 3,3'-diethyl-9-methylthiacarbocyanine by AgCNS.

Age (hr.)	0	4	18	44	290
	1.50	0.87	0.45	0.38	0.38

\* Communication No. 848 from the Kodak Research Laboratories. <sup>1</sup> T. H. James, (a) J. Am. Chem. Soc. **61**, 2379 (1939):

<sup>1</sup> T. H. James, (a) J. Am. Chem. Soc. **61**, 2379 (1939); (b) **62**, 536 (1940); (c) **63**, 1601 (1941); (d) **64**, 731 (1942). diethyl-9-methylthiacarbocyanine which sufficed for silver chloride, because of the action of thiocyanate ion in sedimenting the dye. However, a sharp end point was obtained in the absence of excess thiocyanate ion if the precipitate was first stirred for about ten minutes with two to three times the amount of bromide ion required to cover the surface. The same procedure applied to silver chloride gave results in complete agreement with those obtained by simple titration in the presence of excess chloride ion.

In each of the subsequent experiments, onehalf millimole of silver salt and two millimoles of hydroxylamine were employed. Reaction temperature was  $20.03 \pm 0.03$ °C. Total solution volume was 60 ml. Reaction rates are expressed in terms of the slope of the reaction curve at one-third or one-half completion (the curves in general have an autocatalytic shape), and in terms of the reciprocal of the time required to yield 0.20 ml gaseous reaction product.

The variation of specific surface with age of the silver thiocyanate precipitate is indicated by the dye adsorption data given in Table I. The results

TABLE II. Effect of age of AgCNS on reaction products, pH 10.45.

Age (hr.)	${f Percent} {f N_2}$	Percent N2O
0.25	59	41
.30	58	42
.50	48	52
1.25	43	57
5.25	37	63
17	39	61
66	37.5	62,5

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are quite similar to those obtained for the aging of silver bromide<sup>2</sup> and silver chloride.<sup>3,1(b)</sup> Accompanying the decrease in specific surface with age, but not strictly paralleling it, the nitrogen yield of the hydroxylamine reaction decreases (Table II). The nitrous oxide yield correspondingly increases.

## Effect of Gelatin on the Reduction of Silver Thiocyanate

The data in Table III show the effect of gelatin upon the reaction rate and nitrous oxide yield. Each precipitate was aged 17–20 hours, and then stirred with the specified amount of gelatin for one hour before use. A sharp decrease in the reaction rate is obtained by the first small additions of gelatin. Additions in excess of 2–4 mg have only a small effect. The nitrous oxide yield, on the other hand, passes through a sharp maximum corresponding to 0.2–0.4 mg of gelatin. Further additions produce a continuous decrease (Fig. 1).

Similar results were obtained by the addition of pinacyanol chloride (Table IV). A definite maximum in the nitrous oxide yield is not established in this case, but may exist. A significant decrease in the nitrous oxide yield was not observed until more than 0.5 mg of dye had been added, although the R rate had decreased

TABLE III. Effect of gelatin on the reaction of AgCNS with NH<sub>2</sub>OH.

Gelatin mg	Excess CNS <sup>-</sup> m mole	pН	R <sub>1/3</sub>	1/1	N2O
0.00	0.50	10.2	0.61	0.106	26
.10	.50	10.2	.29	.070	37
.20	.50	10.2	.12	.058	41
.40	.50	10.2	.087	.030	$\bar{37}$
1.00	.50	10.2			22
0.00	.50	10.8	1.9	.80	63
.20	.50	10.8	0.47	.38	70
.40	.50	10.8	.37	.16	76
1.00	.50	10.8	.27	.088	70
4.00	.50	10.8	.088	.033	47
10.00	.50	10.8	.074	.024	31.5
50.00	.50	10.8	.066	.018	18
				· · ·	
0.00	.00	10.45	3.76	4.55	64.5
.50	.00	10.45	0.76	0.62	68
50.00	.00	10.45	.035	.072	25

<sup>&</sup>lt;sup>2</sup> I. M. Kolthoff and A. S. O'Brien, J. Chem. Phys. 7, 401 (1939). <sup>3</sup> I. M. Kolthoff and H. C. Yutzy, J. Am. Chem. Soc.



FIG. 1. Effect of gelatin on reduction of AgCNS. Triangles, N<sub>2</sub>O at pH 10.2; circles, N<sub>2</sub>O at pH 10.8; crosses, R at pH 10.8.

TABLE IV. Effect of pinacyanol on reaction of AgCNS with NH<sub>2</sub>OH.

Dye mg	m moles excess CNS <sup>-</sup>	рН	$R_m$	1/t	Percent N2O
0.00	0.50	10.8	1.9	0.80	63
.10	.50	10.8	1.4	.50	64
.50	.50	10.8	0.22	.33	64
2.50	.50	10.8	.10	.21	60
5.00	.50	10.8	.035	.14	45
0.00	.00	10.45	3.76	4.55	64.5
.50	.00	10.45	0.36	1.66	61.5
5.00	.00	10.45	.52	1.66	53

ninefold. The R rate given in this case is the maximum slope of the reaction curve. These reaction curves are erratic in form, as shown in Fig. 2, and resemble those obtained in the reduction of silver chloride by hydrazine in the presence of 3,3'-diethyl-9-methylthiacarbocy-anine.<sup>4</sup> A monomolecular layer of pinacyanol should cover the surface of this precipitate at less than 0.8 mg of dye, but no minimum reaction rate is obtained up to 5.0 mg of dye.

Much of the pinacyanol originally added was no longer present in the solution at the end of the reaction. Significant chemical destruction of the dye had not occurred, but much dye could be extracted from the silver product by means of

<sup>4</sup> T. H. James, J. Am. Chem. Soc. 62, 1654 (1940).

**<sup>59</sup>**, 1215 (1937).



FIG. 2. Effect of pinacyanol on reduction of AgCNS a pH 10.8. Figures on curves give milligrams of dye.

methanol. Addition of pinacyanol to silver formed in the absence of the dye resulted in an appreciable adsorption of the dye, and the amount was substantially the same, whether the dye was added as pure aqueous solution or as 12M ammonia solution. Hence, it is unlikely that the action of a silver oxide layer at the surface is involved. The silver obtained by reaction in the presence of pinacyanol was more finely divided than that obtained without addition.

#### Mixed Precipitates of Silver Bromide and Thiocyanate

Silver bromide and silver thiocyanate form an incomplete mixture series. Silver thiocyanate dissolves up to three percent silver bromide, and silver bromide dissolves up to ten percent thiocyanate. Intermediate precipitates are composed of the mutually saturated end solutions.<sup>5</sup> In the present investigation, a series of mixed precipitates was prepared by adding to 5.00 ml of 0.10 M silver nitrate in 15 ml total solution, 6.00 ml of 0.10 M mixture of potassium bromide and thiocyanate. The precipitates were aged in contact with the supernatant liquid for 17–20 hours before reaction was carried out at pH 10.45. In Table V,  $R_e$  is a rate value corrected for the

<sup>5</sup> F. W. Kuster and A. Thiel, Zeits. f. anorg. allgem. Chemie **33**, 129 (1902).

difference in volume of gas produced by 1 mole of the silver salt mixture.

The reaction rates do not vary greatly with the change in composition of the precipitate and supernatant liquid. The composition of the gaseous product, however, exhibits a remarkable behavior. The gas remains over 90 percent nitrogen until the thiocyanate reaches 96 percent. After this, the nitrous oxide increases rapidly to the value of 51 percent for the pure thiocyanate.

Table VI gives the results obtained by addition of various amounts of excess thiocyanate, bromide, and iodide to pure, aged silver thiocyanate precipitates 15 minutes before addition of the hydroxylamine. Complete curves for a number of the experiments are given in Fig. 3. It is evident that precipitates to which excess thiocyanate has been added may give the same general reaction rates as those to which excess bromide has been added, but the nitrous oxide yield will be entirely different. There is no connection between pAg and nitrous oxide yield in this case. Added bromide and iodide give identical results within the limits of experimental error.

Table VII gives results obtained when potassium bromide was added to precipitates which had been coated with gelatin or wool violet. The amounts of gelatin or dye added were two or three times those required for a single layer.

#### DISCUSSION

In a preceding paper,<sup>1(d)</sup> evidence was presented that the formation of nitrous oxide is associated with the uncatalyzed reduction of silver ions by hydroxylamine. Nitrogen is the exclusive product of the silver catalyzed reaction involving adsorption of silver ions to the catalyst. In the preceding experiments, therefore, the

TABLE V. Reaction of mixed bromide and thiocyanate precipitates.

Percent Br <sup>-</sup>	$R_{1/2}$	$R_c$	1/t	Percent N₂O
100	0.72	0.72	0.33	0.1
80	1.08	1.08	.40	.2
20	2.05	2.08	.44	2.0
10				3.8
4	2.00	2.12	.52	10.0
1	2.26	2.83	.61	35.0
0	2.00	2.85	.67	51.0

nitrous oxide yield may be taken as a measure of the amount of uncatalyzed reaction.

The reduction of silver bromide in the pHrange 10.2-10.8 involves exclusively, or almost so, the silver catalysis mechanism. Silver thiocyanate in the same pH range, however, may be reduced largely by the non-catalyzed mechanism, and the extent to which this mechanism operates varies greatly with prevailing reaction conditions. The equilibrium pAg of the solution is not an important factor. The solubility product of silver thiocyanate is somewhat less than twice that of silver bromide. Thus, in Table VI, approximately the same pAg would arise in solutions containing 0.1 m mole of potassium bromide or 0.2 m mole of potassium thiocyanate, yet the nitrous oxide yields are 3 percent and 54.5 percent, respectively. On the other hand, surface conditions evidently exert an important and possibly deciding influence.

The specific surface of the thiocyanate precipitates can be determined only roughly from the data at hand. The 18-hour-old precipitate prepared in the absence of excess anion adsorbs about 0.45 mg of 3,3'-diethyl-9-methylthiacarbocyanine. If the same coverage is assumed as TABLE VI. Effect of CNS<sup>-</sup>, Br<sup>-</sup>, and I<sup>-</sup> upon reduction of AgCNS at  $\rho$ H 10.45.

Addition	Amount m moles	R1/3	1/t	Percent N2O
None	_	3.80	4.55	63.5
KCNS KCNS KCNS KCNS	0.10 .20 .50 1.00	2.68 1.88 1.07	0.93 .50 .19	57.7 54.5 40.5 27.5
NaCl	0.50			62.9
KBr KBr KBr KBr KBr KBr	.005 .010 .020 .040 .100 .200	3.78 3.76 3.26 2.50 2.00	2.33 2.33 1.54 0.44 .23	43.5 28 17 7 3 3
KI KI KI	.010 .020 .040	0.39	2.0 2.0 0.80	28 22 6
KBr KCNS	.030) .070)	2.24	.70	19
KBr KCNS	.050) .100}	1.30	.31	19.5
KBr KCNS	.050 .020}	1.92	.74	11.5



FIG. 3. Effect of excess anion on  $AgCNS-NH_2OH$  reaction curves. Curve 1, no addition; curve 2, 0.005 m mole  $Br^-$ ; curve 3, 0.20 m mole  $CNS^-$ ; curve 4, 0.10 m mole  $Br^-$ ; curve 5, 0.04 m mole  $I^-$ .

for silver bromide,<sup>6</sup> this figure gives a specific surface of approximately 4000 sq. cm. If gelatin adsorption occurs on the same basis as with silver chloride, a complete protective layer should be formed by 2-3 mg gelatin.<sup>1(b)</sup>

A comparison of the nitrous oxide-gelatin curves in Fig. 1 shows that a sharp maximum is reached at both pH 10.2 and 10.8. This maximum lies at 0.2 mg of gelatin at the lower pHand 0.4 mg at the higher, both well below the requirements for a complete layer covering the surface. The rate curves show definite breaks at about the gelatin concentrations corresponding to the maximum nitrous oxide yield, but the rates decrease considerably beyond these points before they approach a minimum. The decrease in rate becomes small beyond 2–3 mg of gelatin addition.

Gelatin can reduce the reaction rate in two ways. In the first, adsorption of gelatin to the silver thiocyanate markedly decreases the rate of the direct attack of hydroxylamine upon the silver salt surface and the rate of solution. This action of the gelatin is unfavorable to the non-

TABLE VII. Reduction of coated AgCNS.

	Percent N <sub>2</sub> O from pp. coated		
KBr added m moles	Gelatin ⊅H 10.45	Wool violet pH 10.8	
0	46	58	
0.005	28	_	
.010	19	42	
.050	10	4	

<sup>6</sup>S. E. Sheppard, R. H. Lambert, and R. D. Walker, J. Chem. Phys. 7, 265 (1939).

catalyzed reduction. In the second, adsorption of gelatin to the silver nuclei and at the salt-silver interface decreases the specific rate of the silver catalyzed reaction. The silver nuclei chiefly responsible for the start of the catalyzed reaction are probably formed at relatively unprotected spots on the silver thiocyanate surface. If the amount of gelatin present is sufficient to cover only a fraction of the surface, this may quickly impede the propagation of the catalyzed reaction as the interface reaches the sites of adsorbed gelatin. The decrease in rate of solution and of uncatalyzed attack upon the thiocyanate surface, on the other hand, should be roughly proportional to the amount of surface covered by the adsorbed gelatin. The relative decrease in rate of the catalyzed reaction will thus be greater for small surface coverage. Data previously obtained on the action of gelatin in the reduction of silver chloride by hydroxylamine support this suggestion. A maximum proportion of the uncatalyzed reaction should be reached before the surface of the precipitate is completely covered with gelatin, and further addition of gelatin should favor the catalyzed reaction. The shift in the position of the maximum towards higher amounts of gelatin with increasing pH is expected, since increase in pH relatively favors the uncatalyzed reaction.1(d)

The fact that increases in gelatin addition beyond that required for a complete layer produce increases in the amount of catalyzed reaction participating in the reduction shows that adsorption rates are involved. The silver formed in the attack upon the solid occupies a considerably smaller volume than the original salt. As reaction progresses, the splitting away of the nuclei from the salt along a portion of the boundary, together with disruption of the surface due to solution effects, exposes unprotected surface. Gelatin from solution, however, can act to form a new protecting layer. Thus, a kinetic competition sets in as soon as exposed surface is formed.

The same general considerations may be applied to the effect of pinacyanol upon the reduction of silver thiocyanate. The dye should differ from gelatin only in the degree to which it

relatively influences the rates of the competing reactions. The action of bromide and thiocyanate ions may likewise be explained in the same general way. In this case, since excess of either ion in any amount will prove detrimental to the uncatalyzed reaction, there should be no maximum nitrous oxide yield. Actually, none was observed. The relatively much greater effect of bromide ion is of interest in connection with the observations of Lottermoser and Petersen<sup>7</sup> that a negative silver thiocyanate sol exhibits an essentially smaller adsorption for thiocyanate ions than a negative silver bromide sol does for bromide ions. Silver bromide in the presence of excess bromide ion reacts with hydroxylamine almost exclusively by way of the catalytic mechanism. A relatively small amount of excess bromide ion, added to the thiocvanate precipitate, converts the reaction of that substance largely to the catalytic mechanism. A much larger excess of thiocyanate ion is required to produce a comparable effect. When the solution contains both excess thiocyanate and bromide, the effect of the ions is not additive, but rather competitive. The last three experiments recorded in Table VII show a definite action of the thiocyanate in partially counteracting the effect of the bromide. This suggests that more than mere adsorption of bromide to silver ions is involved. Probably an actual interchange of bromide and thiocyanate ions occurs, resulting in the formation, or partial formation, of a thin layer of silver bromide coating the thiocyanate.

The decrease in specific surface of silver thiocyanate on aging, as indicated by the change in dye adsorption, should have in itself but slight effect upon the product of the reaction with hydroxylamine. The marked increase in nitrous oxide actually observed shows that another more important change has occurred on aging. This may be a sharp decrease in the ability of the aged surface<sup>8</sup> to adsorb thiocyanate ion, or a sharp decrease in the number of active spots at which catalysis centers may be formed.

<sup>&</sup>lt;sup>7</sup>A. Lottermoser and W. Petersen, Zeits. f. physik. Chemie **133**, 69 (1928). <sup>8</sup>J. H. de Boer, *Electron Emission and Adsorption Phenomena* (Cambridge University Press, 1935).