SUMMARY

1. Sorptions of propane and propylene on silica gel and on silica gel metallized with palladium were measured at −25°C., 0°C., and 35°C.

2. The olefin is more strongly sorbed by the metallized surface than by the untreated gel, and it is more strongly sorbed than the paraffin.

3. The results are in reasonably good agreement with the theory of Brunauer, Emmett, and Teller.

REFERENCES

(1) Brunauer, Deming, Deming, and Teller: J. Am. Chem. Soc. **62,** 1723 (1940).
(2) Brunauer, Emmett, and Teller: J. Am. Chem. Soc. **60,** 309 (1938).
(3) Cameron and Reyerson: J. Phys. Chem. **39,** 169 (1935).
(4) Reyerson and Bemmels: J. Phys. Chem. **46,** 31, 36 (1942).
(5) Reyerson and Cameron: J. Phys. Chem. **39,** 181 (1935).
(6) Reyerson and Swearingen: J. Phys. Chem. **31,** 88 (1927).
(7) Reyerson and Wishart: J. Phys. Chem. **41,** 943 (1937).
(8) Scott and Brickwedde: Bur. Standards J. Research **6,** 401 (1931).
(9) Weinhart: Rev. Sci. Instruments **4,** 350 (1933).

INFLUENCE OF AGE AND SURFACE CONDITIONS ON THE REACTIVITY OF CERTAIN PRECIPITATES[1, 2]

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The chemical reactivity of a precipitate may change significantly during aging in contact with the supernatant liquid. The change is usually a regular one which may be related to some alteration in the physical or chemical state of the precipitate. Thus, the rate of initiation of reduction of silver chloride by hydroxylamine decreases regularly with the specific surface (3) and indeed almost exactly parallels it. A marked decrease in the reactivity of silver chloride towards bromide ions occurs when the precipitate is aged (10). Kolthoff and O'Brien observed that when fresh air-dried silver bromide was shaken with a solution of bromine in ethyl bromide or with anhydrous vapors of bromine, a rapid exchange occurred resulting in a heterogeneous distribution of the exchanging (radioactive) constituent through the solid. However, the speed of exchange decreased rapidly with increasing age of the precipitate, and at the same time the abnormally large electrical conductivity of the fresh material decreased rapidly. Hüttig and Garside, on the other hand, found that the reactivity of hydrous ortho-ferric oxide with hydrogen sulfide and hydrochloric acid

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[2] Communication No. 857 from the Kodak Research Laboratories.

exhibited a remarkable periodic variation with age (1). Similar periodic variation was observed in the catalytic activity of the ferric oxide towards the decomposition of hydrogen peroxide. Hüttig and Zörner (2) observed as many as nine peaks in the activity curve within a period of 160 days.

The reactivity of silver chloride towards the developing agent hydroxylamine has been studied in some detail in these Laboratories and this reaction has supplied useful information concerning the mechanism of photographic development. The hydroxylamine reaction can be used conversely to supply information on the surface conditions and aging changes of cupric hydroxide and silver salt precipitates. Preliminary experiments indicate that this reaction may prove useful in a study of the aging of hydrous ferric oxide.

Basically, two reactions occur between silver salts and hydroxylamine. The one is a silver-catalyzed oxidation of the hydroxylamine, which yields nitrogen exclusively or almost exclusively as the gaseous product. The other is an uncatalyzed oxidation which yields chiefly nitrous oxide (6). The reactivity of the precipitates may be studied with respect to both the rate of reaction and the relative occurrence of the two mechanisms. Any nitrous oxide produced by the reaction arises from the uncatalyzed mechanism, and hence measures the relative extent to which this mechanism occurs.

TABLE 1

Effect of age of equivalent silver chloride precipitates on reaction product

pH, 10.2

Age (hours)	0.25	0.50	1.50	17	22
Nitrous oxide (per cent)	37; 36	48	50	47	47

SILVER CHLORIDE

Rate measurements on the reduction of silver chloride by hydroxylamine at pH 7.2, where the initial reaction is uncatalyzed but the subsequent catalyzed reaction overwhelmingly predominates, have already been reported (3, 4). At pH 10.2 the reaction rate is too great to measure, and competition between the two mechanisms is marked. A definite increase in nitrous oxide yield (uncatalyzed reaction) is obtained by aging the silver chloride precipitate (table 1). This effect could not be explained by the decrease in specific surface, but may arise from a sharp decrease in the number of spots at which catalysis centers may form, or from a decrease in mobility of the silver ions within the crystal. Either explanation implies a perfecting of the crystal lattice.

The addition of small amounts of bromide to the aged silver chloride produces a sharp decrease in the yield of nitrous oxide. Analyses of control samples showed that practically all of the added bromide had been taken up by the precipitate during the 25 min. which elapsed before addition of the hydroxylamine[3].

Kolthoff and Yutzy (10) demonstrated that under certain conditions the adsorption of Wool Violet to silver chloride confined the bromide exchange largely

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[3] The author is indebted to A. Ballard and E. S. Perry of these Laboratories for these analyses.

to the surface layer. The results of a series of experiments in which bromide was added to dyed precipitates suspended in a 40-ml. solution are given in table 3.

If the relations which Kolthoff and O'Brien found for silver bromide (9) hold approximately for silver chloride, the specific surface of the precipitates can be calculated from the Wool Violet adsorption. In the presence of excess chloride, 0.14 mg. of dye adsorbed gives a specific surface equivalent to 3.6×10^{-3} millimoles of chloride ion. Kolthoff and O'Brien found that almost twice the amount of Wool Violet is adsorbed by silver bromide in the presence of excess silver ions as in the presence of excess bromide; hence, the 0.23 mg. of dye adsorbed by the silver chloride in the absence of excess chloride does not indicate an increased specific surface. When bromide is added in the absence of excess chloride, the specific surface definitely increases with increased bromide addition, showing

TABLE 2

Effect of bromide ion on reaction of silver chloride with hydroxylamine

AgCl, 0.5 millimole; pH, 10.2

EXCESS CHLORIDE ION	BROMIDE ION		NITROUS OXIDE	NITROUS OXIDE FROM GELATIN-COATED SILVER CHLORIDE
	Added	Removed by AgCl		
millimoles	*millimoles*	*millimoles*	*per cent*	*per cent*
0.00	0.00	0.00	47	43.5
0.00	0.01	0.01	19	
0.00	0.02	0.02	8	32
0.00	0.10	0.099	5	25
0.00	0.20		4	
2.00	0.00		20	
2.00	0.02		5	
4.00	0.00		17	

TABLE 3

Reduction of aged silver chloride coated by Wool Violet

AgCl, 0.50 millimole; pH, 10.2

ADDED CHLORIDE ION	ADDED BROMIDE ION	STIRRING TIME	BROMIDE ION REMOVED	DYE ADSORBED	NITROUS OXIDE
millimoles	*millimoles*	*hours*	*millimoles*	*mg.*	*per cent*
0.00	0.00			0.23	45
0.00	0.10	2.3	0.098	0.25	25
0.00	0.10	1		0.25	31
0.00	0.20	1.2		0.42	23
0.00	0.20	2.5		0.41	22
0.00	0.20	5.5		0.42	
0.00	0.02	5		0.17	29.5
2.00	0.00	6.5		0.14	47
2.00	0.10	2	0.0224	0.13	42
10.00	0.10	7	0.0091	0.14	49

a disintegration of the original particles. Most of the bromide disappears from the solution.

In the presence of excess chloride, the addition of bromide produces no change in the specific surface and only a fraction of the bromide is taken up by the precipitate. The indicated total surface calculated from the bromide uptake is, however, several times greater than that calculated from dye adsorption. Hence, it is probable that even in this case some penetration of bromide below the surface layer occurs.

A comparison of the data in tables 2 and 3 shows that adsorption of Wool Violet by itself has little effect upon the nitrous oxide yield, and hence upon the relative proportion of the catalyzed and uncatalyzed reactions. With no excess chloride, the addition of bromide in small amounts has a much greater effect in the absence than in the presence of Wool Violet. In both cases, however, practically all of the bromide is removed from the solution. The bromide can exert the observed marked effect in the absence of Wool Violet only by forming a sheath of silver bromide around the silver chloride particles. A decrease in silver-ion concentration in the solution is not responsible. All of the bromide is removed from solution prior to the reaction when the additions amount to 0.01–0.02 millimole. Additions of chloride or thiocyanate sufficient to produce an equivalent instantaneous depression of silver ions in solution has a much smaller effect upon the yield of nitrous oxide. Furthermore, in the presence of excess chloride and Wool Violet, much bromide remains in solution, but the change in nitrous oxide is small.

A silver bromide coating of at most a few ionic layers thickness has a pronounced effect upon the reduction mechanism. An addition of 0.02 millimole of bromide decreases the yield of nitrous oxide from 47 per cent to only 8 per cent. This amount of bromide could form a *uniform* sheath only six layers thick, and it is possible that such an excess is necessary to form a complete sheath of only one or two layers. No increase in specific surface was detected. When the silver chloride is first dyed with Wool Violet, however, several times this amount of bromide will not produce a comparable effect. Hence, it is concluded that the presence of Wool Violet favors an uneven penetration of the bromide into the precipitate, disrupting the original particles, or the formation of new particles containing predominantly silver bromide. This conclusion is supported by the increase in specific surface observed in the absence of excess chloride ion. It is noteworthy, further, that the Wool Violet blocks the normal protecting action of excess chloride. The decrease in nitrous oxide yield obtained by adding excess chloride in the absence of Wool Violet does not appear when the precipitate is first coated by the dye.

SILVER THIOCYANATE

The specific surface of a silver thiocyanate precipitate decreases with age in much the same way as that of silver bromide and silver chloride (3, 9, 10). The composition of the product of reaction with hydroxylamine changes with age even more markedly than in the case of silver chloride (table 4). Fairly accurate rate measurements could be made at pH 10.2 in the presence of 0.50 millimole of excess thiocyanate. The initial reaction rate, measured in terms of the reciprocal of the time required for the evolution of 0.2 ml. of gas, showed no change with age (table 5). The rate of reaction at one-third completion, measured by the slope of the curve at this point, showed a definite decrease with age of precipitate. These reaction rates do not have a clear-cut significance, but $1/t$ may be taken as a rough measure of the initial uncatalyzed reaction, whereas $R_{1/3}$ will measure a mixture of the catalyzed and uncatalyzed reactions.

The sharp increase in yield of nitrous oxide shows that the uncatalyzed reaction becomes more prominent as the precipitate ages. Adsorption of excess thiocyanate ions to silver thiocyanate favors the catalyzed reaction (7) and a desorption of thiocyanate on aging is a possible explanation of the observed effect. On the basis of decrease in specific surface, a decrease in the initial reaction rate is to be expected (3). Desorption, on the other hand, would act to increase this rate. Experimentally, a small decrease in rate at most is observed, which suggests that desorption compensates approximately for a decrease in the specific surface in this case. Table 5 shows further that the rate of the catalyzed reaction decreases as the precipitate ages. This could arise either from a decrease in mobility of the silver ions in the crystal or a decrease in the number of spots at the surface at which catalysis centers may form. Each of the factors mentioned would contribute to the observed effect.

TABLE 4

Effect of age of silver thiocyanate on reaction products at pH 10.45

Age (hours)	0.25	0.30	0.50	1.25	5.25	17	66
Nitrous oxide (per cent)	41	42	52	57	63	61	62.5

TABLE 5

Effect of age of silver thiocyanate on reaction rate at pH 10.2

AgCNS, 0.50 millimole; excess CNS^-, 0.50 millimole

AGE	$R_{1/3}$	$1/t$
hours		
0.25	0.90	0.111
0.75	0.88	0.094
2.25	0.62	0.106
17	0.58	0.106
40	0.53	0.098

The addition of small amounts of bromide, iodide, gelatin, and dye to silver thiocyanate precipitates influences markedly the relative proportions of the catalyzed and uncatalyzed reactions. These results have been recorded elsewhere (7).

MERCUROUS CHLORIDE

The action of dyes and gelatin upon the rate of reduction of mercurous chloride (5) differs in one important respect from the corresponding action on silver chloride. In the latter case, the decrease is approximately proportional to the amount of surface covered by the added agent (3). With mercurous chloride, however, a much more pronounced decrease in rate is obtained during coverage of the first few per cent of the total surface, showing that the dyes and gelatin are preferentially adsorbed at the active centers of the precipitate.

CUPRIC HYDROXIDE

The instability of blue cupric hydroxide precipitate is one of its most characteristic properties (12). When precipitation is carried out in the presence of slight excess of alkali, the hydroxide decomposes at room temperature into cupric oxide with an accompanying transition in color through green, brown, and dark brown to black. In this case, the aging process includes a definite chemical change, and the change occurs without formation of any intermediate compound (13).

Hydroxylamine is readily oxidized in alkaline solution by cupric sulfate, yielding nitrous oxide almost exclusively (8, 11). In the present exploratory work with the cupric hydroxide–cupric oxide system, the precipitate was prepared at 25°C. by addition of 5.00 ml. of 0.200 M sodium hydroxide from a pipet to 15.00 ml. of 0.0330 M cupric chloride solution rapidly stirred by a motor-driven paddle. The precipitate was aged for varying times at 25°C. Reduction by hydroxylamine was effected at pH 10.2 and at 20°C. This reaction was carried out in an atmosphere of nitrogen.

The freshly prepared cupric hydroxide reacts at a much greater rate than the cupric oxide formed on aging. A precipitate of intermediate age, containing both components, yields a reaction curve which usually shows a distinct break. Figure 1 illustrates curves obtained from precipitates of several ages. Table 6 gives data obtained from the curves and elsewhere: R_1 is the initial slope of the reaction curves, and R' is the slope of the straight-line portion beyond the break. The fifth column gives values of the intercept, I, obtained by extrapolating the reaction curve beyond the break back to zero time. The extrapolation procedure was used to obtain complete curves for the reduction of cupric oxide. Considerable uncertainty was attached to this procedure for precipitates of ages 0.2–0.5 hr., but extrapolation for the older precipitates was reasonably well defined by the data. The nitrogen yield was calculated from the total volume of gas obtained when reduction to cuprous oxide was complete. Reduction of cuprous oxide to copper proceeded at such a low rate that it could be ignored, and the slight amount of decomposition of hydroxylamine was allowed for by using blanks.

The curves representing the 17- and 113-hr.-old precipitates give evidence of an induction period in the reaction responsible for the curve beyond the break. Reaction curves obtained from precipitates aged for 5 and 65 hr. at 90°C. show unmistakable induction periods (figure 2). The curves beyond the break (which occurs at a gas volume of only 0.09 ml. for the 65-hr. precipitate) are typical of an autocatalyzed reaction. This reaction is almost wholly responsible for the formation of nitrogen as the reaction product, and hence adds one more example to a group of reactions in which catalysis increases the nitrogen yield (6). In this case the catalyst is presumably cuprous oxide, since metallic copper could not be detected in the reaction mixtures.

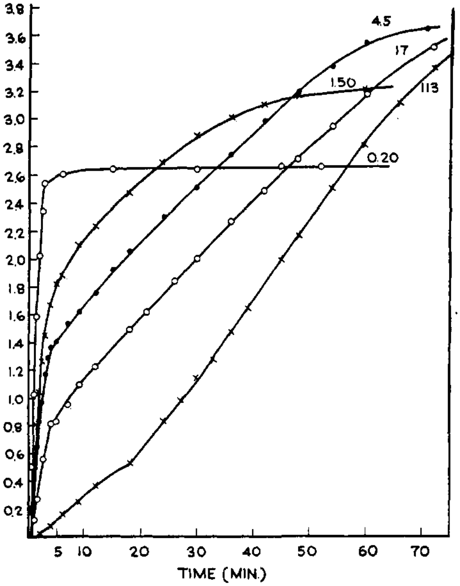

FIG. 1. Reduction of cupric hydroxide-cupric oxide system. Precipitates aged at 25°C.

TABLE 6

Reduction of 0.50 millimole of cupric hydroxide-cupric oxide system by hydroxylamine

pH, 10.2; reaction volume, 60 ml.

AGE OF PRECIPITATE	COLOR	R_1	R'	I (N.T.P.)	TOTAL VOLUME (N.T.P.)	NITROGEN (CALCULATED)
hours						*per cent*
0*				2.34	2.34	0
0.20	Blue-green	1.09		(2.53)	2.64	8
0.50	Green	0.87		(2.40)	2.80	13
1.50	Green-brown	0.63	0.041	1.53	3.26	28
4.50	Brown	0.47	0.051	1.15	3.75	43
17	Dark brown	0.31	0.052	0.75	4.10	54
113	Dark brown	0.035	0.058	0.62	4.25	59

* Cupric chloride added directly to sodium hydroxide containing buffer plus hydroxylamine.

The nitrogen yield appears to be the best quantitative measure of the degree of transition of cupric hydroxide to cupric oxide. The points in a plot of I

against percentage nitrogen fall on a straight line, with the exception of those for the 0.2- and 0.5-hr.-old precipitates. The *I* values for both of these points are very uncertain. The nitrogen yield, therefore, is probably directly proportional to the amount of transition. The rate values, on the other hand, depend not only upon the amount of hydroxide transformed but also upon changes in the surface and structure of the precipitate. This is particularly evident in the

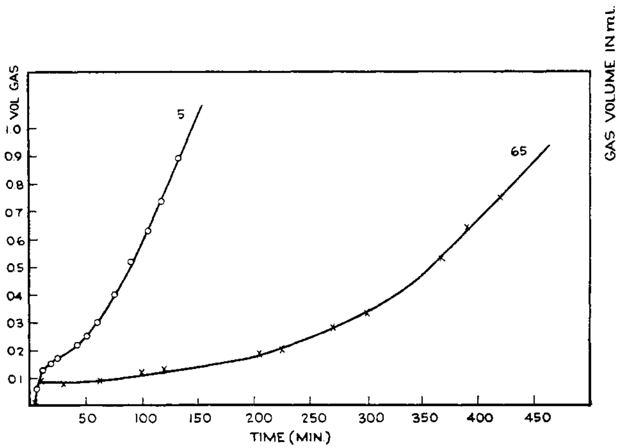

FIG. 2. Reduction of cupric hydroxide–cupric oxide system. Precipitates aged at 90°C

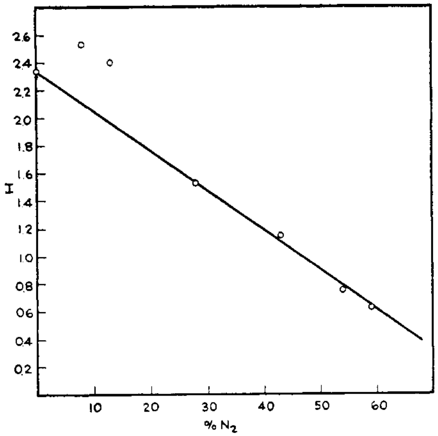

FIG. 3. Plot of *I* against per cent nitrogen

results obtained with precipitates aged at 90°C. The R_i values for the 25°C. precipitates do not vary linearly with the amount of cupric hydroxide, but follow rather accurately the exponential function

$$R_i = dx/dt = e^{kx}$$

for precipitates of intermediate ages.

SUMMARY

Information concerning structural and surface changes in certain precipitates is obtained from a study of their reactivity with hydroxylamine. Silver chloride and silver thiocyanate yield an increase in nitrous oxide upon aging, indicating a perfecting of the lattice. Small amounts of bromide ion produce marked decreases in nitrous oxide. Silver chloride precipitates coated with Wool Violet show much smaller decreases when comparison is made at the same uptake of bromide by the precipitate. Blue cupric hydroxide reacts rapidly with hydroxylamine at pH 10.2, yielding almost wholly nitrous oxide. As the precipitate ages, the initial reaction rate decreases. A sharp break develops in the reaction curve, corresponding to the presence of cupric oxide. Nitrogen is formed in the reaction of cupric oxide with hydroxylamine, and the percentage of nitrogen is a measure of the amount of transition to cupric oxide.

REFERENCES

(1) Hüttig, G. F., and Garside, H.: Z. anorg. allgem. Chem. **179,** 49 (1929).
(2) Hüttig, G. F., and Zörner, A.: Z. anorg. allgem. Chem. **184,** 180 (1929).
(3) James, T. H.: J. Am. Chem. Soc. **62,** 536 (1940).
(4) James, T. H.: J. Am. Chem. Soc. **62,** 1649 (1940).
(5) James, T. H.: J. Am. Chem. Soc. **63,** 1601 (1941).
(6) James, T. H.: J. Am. Chem. Soc. **64,** 731 (1942).
(7) James, T. H.: J. Chem. Phys. **10,** 464 (1942).
(8) Knorre, G. v., and Arndt, K.: Ber. **33,** 40 (1900).
(9) Kolthoff, I. M., and O'Brien, A. S.: J. Chem. Phys. **7,** 401 (1939).
(10) Kolthoff, I. M., and Yutzy, H. C.: J. Am. Chem. Soc. **59,** 1215 (1937).
(11) Kurtenacker, A., and Wengefeld, F.: Z. anorg. allgem. Chem. **140,** 301 (1924).
(12) Weiser, H. B.: *Inorganic Colloid Chemistry*, Vol. II. John Wiley and Sons, Inc., New York (1935).
(13) Weiser, H. B., Milligan, W. O., and Cook, E. L.: J. Am. Chem. Soc. **64,** 503 (1942).