XIII.—*The Rôle of Protective Colloids in Catalysis. Part I.*

By Thomas Iredale.

The effect of protective colloids in inhibiting the catalytic decomposition of hydrogen peroxide by colloidal platinum has already been noted by Gróh (*Zeitsch. physikal. Chem.*, 1914, **88**, 414), who found that they appeared to follow the order of Zsigmondy's "gold number" series (*Zeitsch. anal. Chem.*, 1901, **40**, 697; "Colloids and the Ultramicroscope," 1914, 79) in their activity in this respect. It appeared desirable, however, to extend investigations in this direction, as the experimental results obtained by Gróh were too few to permit of a general statement as to the relative effects of different protective colloids. A number of these colloids have now been examined in this regard, and it has been found that, in general, the stronger a substance is as a protective colloid the greater will be its inhibition of catalytic activity, and that a substance like sucrose, which is without protective effect, is likewise without inhibitive effect.

Now in view of the circumstances in which the protective colloids are examined in the two cases—Zsigmondy's coagulation method and Gróh's catalytic method—there is nothing altogether surprising in these results. From superficial considerations they might almost be anticipated, and the author was inclined to believe that they might throw considerable light not only on the mechanism of protective action, but also on the processes involved in the hydrogen peroxide decomposition. Unfortunately, owing to war conditions, Gróh's paper itself was not available, and the author had to be content with abstracts (A., 1915, ii, 239; *Chem. Abstracts*, 1915, 7). From these it does not appear that Gróh advanced any thorough argument to account for his results, but he seems to have endeavoured to obtain a relation between the gold number of protective colloids and the extent of their inhibitive effect, the significance of which seems, at present, a little obscure.

It is necessary to examine the analogy more thoroughly. In this connexion some recent remarks made by workers in this field are of interest. Bancroft (*J. Physical Chem.*, 1917, **21**, 775) considers that a substance like gelatin may increase the degree of dispersity of the catalyst, thus exposing a larger surface with increased catalytic activity, but that this effect may be more than counterbalanced by the presence of the gelatin itself, which hinders the

adsorption of the hydrogen peroxide. There is no evidence that protective colloids increase the degree of dispersity of a metal sol already formed, and in view of Rusznyak's work (*Zeitsch. physikal. Chem.*, 1913, **85**, 681) on the decreased catalytic activity with increased dispersity, Bancroft's argument seems scarcely reasonable.

Rideal (*J. Amer. Chem. Soc.*, 1920, **42**, 749) considers that diffusion is the chief factor concerned in the rate of decomposition of hydrogen peroxide, and argues against the idea of a colloid-complex formation. If this is the case, why should a strong protective colloid inhibit to a greater extent than a weak one? What part can diffusion play in the ordinary method of measuring the value of protective colloids as announced by Zsigmondy? The change from red to blue in the colour of gold sols is assumed to be due to a union of the gold particles after their charges have been neutralised by the adsorption of certain ions. Protective colloids may hinder this change for one or other of two reasons. It may be that after the neutralisation of their charges the gold particles are prevented from uniting owing to the presence of the protective colloid. On this theory it is difficult to see where the analogy exists in the case of the catalytic process. If we assume, however, that the protective colloid hinders the adsorption of the ions that would bring about the coagulation, then the analogy is quite complete. The rate of decomposition of hydrogen peroxide is probably determined by a number of factors of which adsorption is undoubtedly one of the chief. Anything which hinders the adsorption of the hydrogen peroxide by the catalyst will retard the velocity of reaction as measured in the usual way, and a strong protective colloid which hinders the adsorption of ions better than a weak one, may also hinder the adsorption of the hydrogen peroxide more efficiently. It remains to be seen, however, if the gold number is really expressive of these relations.

Zsigmondy ("Colloids and the Ultramicroscope," 1914, 150) has endeavoured to follow the mechanism of protective action under the ultramicroscope. The assumed union of the gold and gelatin ultramicrons is followed by decreased mobility in the former, except at a certain concentration of gelatin, below which there does not seem to be any retardation in the movements of the gold particles. It will be seen later that the inhibitive effect of gelatin is noticeable at much lower concentrations than the critical one mentioned by Zsigmondy, and this inhibition cannot be due, therefore, to any decreased mobility in the particles of the catalyst. As far as the Brownian movement is concerned, however, the part played by it in the catalysis is still somewhat obscure.

Bredig (*Zeitsch. physikal. Chem.*, 1901, **37**, 14) has shown that the adsorption of poisons by the catalyst follows the logarithmic law, and it was anticipated that the adsorption of protective colloids might also obey the same law. From results obtained with gelatin at very low concentrations, it appears that the process is more complicated than a simple calculation can possibly account for, owing to the continual subdivision of the gelatin ultramicrons over a certain range of dilution.

The results of experiments on the poisoning of protected metals will be made available in a later communication.

Experimental.

The hydrogen peroxide used in all these experiments was carefully purified by distillation under diminished pressure. The colloidal platinum solutions were prepared by Bredig's method, using a current of 110 volts and 10—12 amperes, the temperature of the water being kept below 25°. Solutions made by this method may be diluted to the extent desired, and after allowing the larger particles to settle, may be used directly without filtering. They appear, however, to be much more sensitive than filtered ones, and cannot be used for very exact work where it is desired to follow the course of a reaction with the maximum of accuracy. The velocity constant falls slightly during the reaction, instead of rising, as is usually the case.

The solutions of protective colloids were prepared by simple dissolution of the materials in water, adopting the usual procedure for gelatin and starch. In the case of gum tragacanth and egg-albumin, which gives extremely turbid solutions, a known weight of material was dissolved as much as possible in water, and the amount of undissolved matter ascertained after filtration. With a knowledge of the weight of substance in the filtrate it could then be diluted to the concentration required. The concentration of protective colloids when first prepared was 0·04 per cent., and lower concentrations were obtained merely by dilution from this strength.

The initial concentration of the hydrogen peroxide in all the experiments was $M/40$. The concentration of the platinum solutions was the same throughout any one series.

All the reactions were carried out at 25°, and in every instance the platinum solutions on admixture with the protective colloids were allowed to remain for fifteen minutes at the temperature of the experiment before the addition of the hydrogen peroxide. At different intervals 10 c.c. of the reaction mixture were titrated, after addition to dilute sulphuric acid, with standard permanganate

(about $N/40$). It was not found necessary to apply a correctic to the titrations for organic matter present as the concentration c the latter was apparently too small to affect the results.

The velocity constant was calculated from the usual formula:

$$k = 0{\cdot}4343\ k_1 = \frac{1}{t}\log_{10}\frac{a}{a-x}$$

(t in minutes, and $a-x$ in terms of c.c. of potassium permar ganate).

The values of k given in the tables are the progressive one obtained during any reaction, and the mean of these in each cas gives the same result on comparison as the time for 50 per cent decomposition.

The ratio values were calculated by taking the velocity constan with unprotected metal as unity.

Table I.

Protective Colloid Preparations: Six Days Old.

Series.	Protective colloid.	k.			Mean.	Ratio.
I.	none	0·026,	0·023,	0·023	0·024	1
	0·01% gelatin	0·0043,	0·0043,	0·0044	0·0043	0·17
	,, glue	0·0046,	0·0043,	0·0041	0·0043	0·17
	,, egg-albumin	0·0055,	0·0052,	0·0050	0·0052	0·22
	,, gum arabic	0·014,	0·012,	0·012	0·013	0·54
	,, sucrose	0·027,	0·025,	0·025	0·025	1
II.	none	0·039,	0·038,	0·037	0·038	1
	0·001% gelatin	0·0074,	0·0082,	0·0078	0·0078	0·20
	,, glue	0·0080,	0·0078,	0·0077	0·0078	0·20
	,, egg-albumin	0·013,	0·012,	0·012	0·012	0·32
	,, gum arabic.	0·032,	0·031,	0·031	0·031	0·82
	,, sucrose	0·038,	0·036,	0·036	0·037	1

Table II.

Preparations One Day Old.

Series.	Protective colloid.	k.			Mean.	Ratio.
I.	none	0·057,	0·052,	0·056	0·055	1
	0·01% gelatin	0·0058,	0·0061,	0·0060	0·0059	0·11
	,, glue	0·0071,	0·0073,	0·0071	0·0072	0·13
	,, egg-albumin	0·0093,	0·0095,	0·0094	0·0094	0·17
	,, gum arabic	0·037,	0·035,	0·034	0·035	0·64
II.	none	0·025,	0·024,	0·025	0·025	1
	0·001% gelatin	0·0044,	0·0043,	0·0045	0·0044	0·18
	,, glue	0·0055,	0·0059,	0·0053	0·0056	0·22
	,, egg-albumin	0·0068,	0·0072,	0·0071	0·0070	0·28
	,, gum arabic	0·020,	0·021,	0·020	0·020	0·80

From these results it is evident that the inhibitive effect is in the order gelatin and glue>egg-albumin>gum arabic>sucrose, which does not appear to affect the reaction at all.

This order is also followed in Zsigmondy's coagulation experiments, but the author has not been able to discover any exact relationship between the gold numbers of these colloids and their inhibitive activity as indicated in the ratio table.

Subsequent determinations of the gold number by the usual method (Zsigmondy, *loc. cit.*) gave values of 0·006 and 0·008 for the samples of gelatin used, and 0·2 for gum arabic, so that the author was not working with materials showing any great anomalies in this respect.

The gold numbers seem, therefore, to be only a useful guide to enable one to predict the probable order of inhibitive activity.

The protective colloids are themselves without appreciable action on hydrogen peroxide. Bredig (*Zeitsch. physikal. Chem.*, 1899, **31**, 342) showed this in the case of gelatin, and it has been found that the stability of a hydrogen peroxide solution is not appreciably affected by the addition of protective colloids of the concentrations indicated in any of these tables.

The extent of the inhibition produced by some of the weaker protective colloids is shown in the following table:

TABLE III.

Preparations Two Days Old.

Series.	Protective colloid.	*k*.			Mean.	Ratio.
I.	none	0·080,	0·083,	0·086	0·083	1
	0·01% gum tragacanth	0·030,	0·029,	0·027	0·028	0·34
	,, dextrin	0·032,	0·031,	0·030	0·031	0·37
	,, starch	0·042,	0·042,	0·040	0·041	0·50
	,, gum arabic	0·044,	0·044,	0·040	0·043	0·52
II.	none	0·017,	0·018,	0·018	0·018	1
	0·01% egg-albumin	0·0036,	0·0038,	0·0039	0·0038	0·21
	,, tragacanth	0·0078,	0·0074,	0·0073	0·0075	0·42
III.	none	0·017,	0·018,	0·019	0·018	1
	0·001% egg-albumin ...	0·0057,	0·0058,	0·0056	0·0057	0·32
	,, tragacanth	0·012,	0·013,	0·013	0·013	0·72
IV.	none	0·017,	0·018,	0·019	0·018	—
	0·01% sodium oleate ...	0·021,	0·023,	0·023	0·023	—
	0·005% ,, ,, ...	0·0130,	0·0130,	0·0131	0·0130	—
	0·001% ,, ,, ...	0·0127,	0·0129,	0·0127	0·0128	—
	0·0025% ,, ,, ...	0·0150,	0·0152,	0·0151	0·0151	—

From these results it is evident that tragacanth inhibits to a less extent than egg-albumin, but is somewhat more effective than dextrin, which is more effective than starch and gum arabic.

Sodium oleate behaves abnormally, as it must be completely hydrolysed at these low concentrations, and the velocity constant will rise owing to the presence of hydroxyl ions. It is interesting to observe, however, that on dilution from 0·01 per cent. concentration the protective effect of the soap begins to dominate the situation, and the velocity constant therefore falls, but rises again on further dilution of the protective colloid. This observation is of great importance, as it shows that the protective action of soaps on gold sols is not due to the stabilising effect of the hydroxyl ions alone—the concentration of the latter in a 0·01 per cent. sodium oleate solution could not be greater than $N/3000$—but more probably in greater part to the acid–soap residue which is more complex, perhaps, than is generally realised.

Gelatin appears to be active as an inhibitor at extremely low concentrations. With a platinum solution of medium concentration (about 1/30,000 gram-atoms per litre) the following results were obtained:

TABLE IV.

Series.	Protective colloid.	k.	Mean.
I.	none	0·0148, 0·0152, 0·0151, 0·0154	0·0151
	0·005% gelatin	0·0028, 0·0026, 0·0026, 0·0027	0·0027
	0·001% „	0·0032, 0·0032, 0·0031, 0·0029	0·0031
	0·0001% „	0·0045, 0·0044, 0·0041, 0·0040	0·0043
	0·00005% „	0·0050, 0·0049, 0·0050, 0·0051	0·0050
	0·00001% „	0·0105, 0·0108, 0·0108, 0·0108	0·0107
	0·000005% „	0·0137, 0·0142, 0·0141, 0·0139	0·0140
	0·000001% „	0·0149, 0·0148, 0·0152, 0·0154	0·0151
II.	none	0·0158, 0·0161, 0·0167, 0·0162	0·0162
	0·001% gelatin	0·0030, 0·0032, 0·0030, 0·0029	0·0030
	0·0001% „	0·0043, 0·0039, 0·0038, 0·0038	0·0039
	0·00005% „	0·0050, 0·0047, 0·0045, 0·0047	0·0048
	0·00001% „	0·0108, 0·0110, 0·0114, 0·0117	0·0112
	0·000005% „	0·0123, 0·0123, 0·0129, 0·0133	0·0127
	0·000001% „	0·0155, 0·0156, 0·0159, 0·0160	0·0158

Series I and II were carried out with different samples of gelatin.)

The most striking fact about these results is the gradual rise of the velocity constant with diminishing gelatin concentrations down to 0·00005 per cent., and the rapid rise on further dilution of the protective colloid.

Now Menz (*Zeitsch. physikal. Chem.*, 1909, **66**, 129) found that the protective action of gelatin increased on dilution, but the results were usually dependent on the mode of preparation of the original solution. It seems not improbable, however, that on diluting a gelatin solution of low concentration, the larger gelatin ultramicrons split into smaller ones, and these being more strongly

adsorbed by the gold or platinum particles will partly make up for the decreased concentration of the protective colloid. Hence the velocity constant will only rise very slowly until this subdivision process ceases, when further dilution of the protective colloid will now bring about its more rapid elevation.

Summary.

(i) The inhibitive effect of protective colloids on the catalytic decomposition of hydrogen peroxide by colloidal platinum has been examined in a number of instances.

(ii) It has been found that the stronger a substance is as a protective colloid the greater will be its inhibition of catalytic activity.

(iii) In the case of a strong protective colloid like gelatin, the inhibitive effect is noticeable at very great dilution, for example, 0·000005 per cent., or one part in twenty million parts of water.

(iv) The inhibition is explained on the ground of selective adsorption resulting in a decreased concentration of hydrogen peroxide at the platinum surface, and a consequent fall in the value of the velocity constant.

(v) There is no precise relation between the gold numbers of protective colloids and the extent of their inhibition.

(vi) The reaction may be used not only to detect adsorption effects, but probably, also, changes in state of the protective colloid owing to the subdivision of its ultramicrons.

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