CATALYSIS BY SILVER, BASIC CATALYSIS, AND CATALYSIS BY UNDISSOCIATED MOLECULES OF ACETIC ACID IN THE REDUCTION OF SILVER ION BY FERROUS ION

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The reaction between silver ion and ferrous ion has been studied by Dhar (2) and by Roberts and Soper (16). Noyes and Brann (15) determined the equilibrium constant of the reaction:

$$Fe^{++} + Ag^{+} \rightleftharpoons Fe^{+++} + Ag$$

The present authors find that the reaction between silver ion and ferrous ion exhibits certain unique features from the point of view of the mechanism of general acid–base catalysis as conceived by Brønsted (1), and have therefore studied the reaction from various aspects.

CATALYSIS BY SILVER AND THE ORDER OF THE REACTION

The catalytic role of silver has been reported by Sheppard (17). In a series of papers James (3, 4, 5, 6, 7) has demonstrated that, in the reduction of silver salts, the reduced silver in the form of fine particles acts as a catalyst. Owing to a continuous flux in the quantity of the heterogeneous autocatalyst (*viz.*, the fine particlesof silver) produced in the reaction, it becomes extremely difficult to determine the exact nature of the specific reaction rate constant. A direct determination of the velocity constant has been made by Krishna and Ghosh in the reaction between silver acetate and resorcinol and between silver tartrate and resorcinol (11, 12). In the reaction between silver ion and ferrous ion, the authors have already discussed the role of catalytic silver and the nature of the specific reaction rate constant (13, 14). In the present paper they have studied the reaction with special reference to the role of hydrogen ions, basic ions, and undissociated molecules of acetic acid. The effect of variation in the ionic strength of the medium upon the reaction velocity has also been studied.

EXPERIMENTAL

Since the reduction of silver ion is a strongly photocatalytic reaction, the reaction was carried out in a bottle made of dark Jena glass. It is necessary to point this out, since others (2, 16) who have studied this reaction have neglected this precaution. Our conclusions are, therefore, applicable with certainty to the dark reaction only.

The reaction is started by adding a known volume of standard ferrous sulfate solution to a buffered or nonbuffered solution of silver nitrate, silver sulfate, or silver acetate kept in the dark-glass bottle and maintained at a constant temperature. The buffer used is a mixture of sodium acetate and acetic acid.

From this reaction mixture 10-ml. portions are taken out at definite intervals of time and added to a known volume of a standard solution of potassium sulfocyanide. The latter removes silver ions and thus stops the reaction. From the supernatant filtrate 5 ml. is removed and added to 5 ml. of a standard silver nitrate solution. The excess of silver nitrate solution is then titrated against a standard solution of potassium thiocyanate in the presence of ferric alum as indicator. Titrations are carried out with a microburet.

Table 1 shows the nature of the bimolecular velocity constant obtained in a typical case. A discussion of the exact nature of the specific reaction rate constant and of the order of the reaction is not relevant for the present purpose, particularly because these matters have been dealt with in previous papers (9, 13, 14). The actual magnitude of the bimolecular velocity constant varies with time, owing to catalysis by silver. For the purpose of comparison, therefore, the maximum value of the velocity constant obtained in a given reaction has been taken as the measure of the velocity of the reaction.

TABLE 1

The bimolecular velocity constant for the reduction of silver ion by ferrous ion

Reaction mixture: 0.02 *M* acetic acid, 0.0025 *M* sodium borate, 0.005 *M* ferrous sulfate, 0.005 *M* silver nitrate; temperature = 30°C.; pH = 7.00

TIME	VOLUME OF 0.01 *N* KCNS USED	BIMOLECULAR VELOCITY CONSTANT $K = \frac{1}{t}\frac{x}{a(a-x)}$
min.	*ml.*	
0	2.10	
10	2.08	0.0009694
20	2.00	0.002124
30	1.96	0.002850
50	1.80	0.002944
80	1.68	0.002846
120	1.59	0.002522
180	1.53	0.001916
Infinity	0.52	

Table 1 shows that the value of the specific reaction rate constant increases with time, owing to catalysis by silver, which is a function of the primary particles of silver formed in the reaction. After reaching a maximum, the reaction constant begins to decrease, owing to the removal of primary particles as these coalesce to form secondary (11) and tertiary ones.

DEPENDENCE OF REACTION RATE UPON ACETATE-ION CONCENTRATION

Table 2 contains a summary of the results obtained in the reaction between silver nitrate and ferrous sulfate in the presence of varying concentrations of acetate ion and a fixed amount of acetic acid.

Similar results were obtained with silver sulfate and silver acetate.

It might appear that the increase in velocity is due to an increase in hydroxyl-ion concentration rather than acetate ions. In order to make the velocity independent of hydroxyl-ion concentration, the experiments were repeated with buffers of constant acid–base ratio but varying total concentration of the buffer.

The results in table 3 were obtained with silver acetate as the source of silver ions. This table proves conclusively that the reaction between silver ion and ferrous ion is catalyzed by acetate ions. In other words, it is a case of basic catalysis (1, 8), where anions of weak acids are involved in catalysis.

TABLE 2

Reaction between silver nitrate and ferrous sulfate in the presence of varying concentrations of acetate and a fixed amount of acetic acid

0.005 *M* silver nitrate; 0.005 *M* ferrous sulfate; 0.02 *M* acetic acid; temperature = 30°C.

CONCENTRATION OF ACETATE IONS, C_A	pH	MAXIMUM VALUE OF THE BIMOLECULAR VELOCITY CONSTANT, *K*
M		
0.05	5.16	0.01806
0.10	5.59	0.02450
0.15	5.72	0.03284
0.20	5.85	0.04230
0.30	6.09	0.06222
0.40		0.07722
0.60		0.15900

TABLE 3

*Results obtained with silver acetate**

C_{HA}/C_A = 9; TEMPERATURE = 35°C.; pH = 3.72		C_{HA}/C_A = 2.33; TEMPERATURE = 35°C.; pH = 4.23	
C_A	*K*	C_A	*K*
M		*M*	
0.01	0.02216	0.03	0.02399
0.02	0.05553	0.06	0.06887
0.04	0.12990	0.12	0.11540

* C_{HA} = concentration of acetic acid; C_A = concentration of acetate ions.

CATALYSIS BY BORATE AND CARBONATE IONS

If to the reaction mixture containing silver ions and ferrous ions, a crystal of sodium carbonate or borate is added, the reaction velocity is greatly increased. No quantitative experiments (except in a few cases, see table 1), however, can be carried out, owing to the high insolubility of silver borate and silver carbonate. It appears, therefore, that the reaction between silver ion and ferrous ion is a case of general basic catalysis.

ANTICATALYTIC ACTIVITY OF HYDROGEN IONS

An increase in the concentration of hydrogen ions leads to a retardation in reaction velocity. This effect is observable if the concentration of acetic acid is increased in the absence of sodium acetate (see table 4).

Similar results were obtained with sulfuric acid. Sulfuric acid (0.01 *N*) completely checks the reaction in the case of the reduction of silver sulfate in the absence of sodium acetate. It is therefore obvious that hydrogen ions are strongly anticatalytic for this reaction. This conclusion is in direct contradiction to that reached by others (2, 16).

TABLE 4

Effect of hydrogen ions on the reaction velocity

0.005 *M* silver nitrate; 0.005 *M* ferrous sulfate; no sodium acetate; temperature = 30°C.

C_{HA}	pH	*K*
M		
0.02	4.83	0.001023
0.04	2.95	0.0008641
0.08	2.94	0.0000000 (no reaction)

TABLE 5

Effect of acetic acid upon the reaction velocity, when added in the presence of a constant amount of sodium acetate

0.005 *M* silver nitrate; 0.005 *M* ferrous sulfate; 0.05 *M* sodium acetate; temperature = 30°C.

C_{HA}	pH	*K*
M		
0.02	5.16	0.018060
0.05	4.80	0.003911
0.08	4.55	0.015050
0.12	4.48	0.03327
0.22	4.17	0.03327
0.42	4.00	0.059840

TABLE 6

Effect of variation in the ionic strength upon the reaction velocity

0.005 *M* silver nitrate; 0.005 *M* ferrous sulfate; 0.02 *M* acetic acid; 0.05 *M* sodium acetate; temperature = 30°C.

$\Delta\mu = \Delta(\frac{1}{2}\Sigma mc^2)$	ELECTROLYTE ADDED	ΔK
0.20	KNO_3	−0.009410
0.80	KNO_3	−0.010476
1.85	$Mg(NO_3)_2$	−0.010730

EFFECT OF THE ADDITION OF ACETIC ACID IN THE PRESENCE OF SODIUM ACETATE; CATALYSIS BY UNDISSOCIATED MOLECULES OF ACETIC ACID

The fact of paramount importance in this connection is that acetic acid works as a negative catalyst only in the absence of sodium acetate, while in the presence of sodium acetate it acts as a positive catalyst. This we interpret to mean that the undissociated molecules of acetic acid also act as a positive catalyst.

It will be observed in table 5 that there is at first a decrease and then an increase in the reaction velocity when acetic acid is added in the presence of a con stant amount of sodium acetate. This presence of a minimum is of extreme importance in connection with catalysis by the undissociated molecule of acetic acid (see the discussion). At this point a number of objections may be raised. It may be argued that our assignment of a catalytic role to acetate ions and undissociated molecules of acetic acid is only illusory, for an increase in the reaction velocity might well be due to a variation in the ionic strength of the medium or else might have been brought about by variation in the size and number of primary particles when different catalysts are added. Before we meet such objections, it is necessary to summarize the effect of variation in the ionic strength upon the reaction velocity when electrolytes are added (table 6).

$\Delta K/\Delta\mu$ is negative. This invalidates all arguments which ascribe a positive increment in reaction velocity to a salt effect. Therefore, the increase in velocity when the acetate-ion concentration is increased is due to its specific nature (i.e., its basicity). It may be further pointed out that 10 ml. of $M/60$ thorium nitrate in the reaction mixture completely stops the reaction. This is due to the fact that thorium ion behaves as an acid and its anticatalytic activity is like that of hydrogen ions.

DISCUSSION

It is worthwhile to consider the mechanism of the salt effect in some detail. Brønsted (1) considers three kinds of salt effects: (*1*) a primary exponential salt effect, (*2*) a primary linear salt effect, and (*3*) a secondary salt effect. For our purpose we need not consider the primary linear salt effect, which is peculiar to reactions between neutral molecules or between a neutral molecule and an ion. The primary exponential salt effect is given by the formula (valid for water at 25°C.)

$$h = KC_AC_B \times 10^{Z_A Z_B \sqrt{\mu}}$$

where h is the velocity of the reaction, C is the concentration of the reacting ions, Z is the charge on the ions, and μ is the ionic strength of the medium. It is obvious that Δh will be negative (if $\Delta\mu$ is positive) for ions of opposite charges, and positive for ions of similar charges. The equation is of great utility in tracing the reaction mechanism in ionic systems, and Krishna (10) has employed it in elucidating the mechanism of the reaction between ferric ion and stannous ion. In the present case, both the reactants being positive ions, a positive salt effect should have been obtained. As a matter of fact, the reverse is the case.

THE NEGATIVE SECONDARY SALT EFFECT

The real explanation of the negative salt effect observed in the present case lies in the fact that the dissociation of acetic acid increases in the presence of electrolytes (1) with a consequent increase in the concentration of hydrogen ions, which decrease the reaction velocity. The thermodynamic equilibrium constant for acetic acid is given by

$$K = \frac{C_{\text{A}} C_{\text{H}}}{C_{\text{HA}}} \cdot \frac{f_{\text{A}} f_{\text{H}}}{f_{\text{HA}}}$$

where C is the concentration and f the activity coefficient. When μ increases, the activity coefficients decrease and there is a consequent increase in the dissociation of acetic acid. The hydrogen-ion concentration therefore increases, and a decrease is observed in the reaction velocity. This negative salt effect has, perhaps, never been reported in the literature. On the addition of electrolytes the concentration of acetate ions is also increased, but the positive catalysis by acetate ions is more than balanced by the negative catalysis by hydrogen ions. Hence the negative salt effect is observed upon the addition of electrolytes.

The second objection will now be considered. Do these external catalysts (*viz.*, the acetate ions and the undissociated molecules of acetic acid) really act as homogeneous catalysts or do they play only a subsidiary role by altering the nature and extent of the catalytic surface? It is impossible to exclude the presence of silver from the reaction mixture, since silver is a reaction product. Consequently it is not possible to study separately the effect of homogeneous catalysts.

Two points, however, appear to be decisive. Firstly, we find that in the presence of catalyzing agents (e.g., acetate ions) the induction period is considerably shortened and in fact can be indefinitely reduced by increasing the quantity of the homogeneous catalyst. This lends support to the view that these factors work independently of silver, for an induction period means a period of very slow reaction in almost complete absence of silver particles. An induction period therefore implies an interval of homogeneous reaction when the catalytic surface is negligibly small, and a shortening of the induction period means that the catalyzing agents (other than silver) are working independently of silver.

Secondly, we find that on the addition of acetic acid in the presence of a constant amount of sodium acetate, at first there is a decrease (see table 5) in the value of K, and after a minimum is reached, there is again an increase. Further work is being carried out in this laboratory in this connection (to be published later), and we find that there is always a minimum point in the value of K when acetic acid is added in the presence of a constant amount of sodium acetate.

It is, *a priori*, improbable that the catalytic surface should at first decrease and then increase as the amount of acetic acid is increased. On the other hand, our theory of homogeneous reaction explains it mathematically as follows:

The overall bimolecular velocity constant can be split up into two terms—one heterogeneous and the other homogeneous—and we can write:

$$K = K_{\text{homo.}} + K_{\text{hetero.}} \tag{1}$$

In the presence of acetic acid and sodium acetate the $K_{\text{homo.}}$ itself is made up of three terms—one due to the catalytic activity of undissociated molecules of acetic acid, the second due to that of acetate ions, and the third due to hydrogen ions (this last term being negative). We can, therefore, write

$$K_{\text{homo.}} = K_1(1 - a)C + K_2(C_A + aC) + K_3aC \tag{2}$$

where a is the degree of dissociation of acetic acid, $(1 - a)$ is the fraction of the undissociated molecules of acetic acid, C_A is the concentration of acetate ions (this being constant), and C is the concentration of acetic acid. It is to be noted that the value of K_3 is negative, since hydrogen ions act as an anticatalyst. Writing the ordinary dissociation constant of acetic acid in the presence of sodium acetate we have:

$$K = \frac{aC(aC + C_A)}{C(1 - a)}$$

or

$$C = \frac{K(1 - a) - aC_A}{a^2}$$

Substituting the value of C in equation 2 we have

$$K_{\text{homo.}} = \frac{K_1(1 - a)\,[K(1 - a) - aC_A]}{a^2} + \frac{K_2[K(1 - a) - aC_A]}{a} + \frac{K_3[K(1 - a) - aC_A]}{a} + K_2C_A$$

$$= \phi(a), \text{ say.} \tag{3}$$

The first condition for a minimum for $K_{\text{homo.}}$ is that

$$\frac{d\phi(a)}{da} = 0$$

Differentiating equation 3 and equating it to zero we have

$$\frac{d\phi(a)}{da} = -\frac{2K_1K}{a^3} + \frac{2K_1K}{a^2} + \frac{K_1C_A}{a^2} - \frac{K_2K}{a^2} - \frac{K_3K}{a^2} = 0$$

whence

$$a = \frac{2K_1K}{2K_1K - K_2K - K_3K + K_1C_A}$$

Now since the anticatalytic activity of hydrogen ions is much greater than the positive catalytic activity of acetate ions (0.01 N sulfuric acid completely stops the reaction in the absence of sodium acetate), we have

$$|K_2| < |K_3|$$

and since K_3 is negative, $-K_3K > 0$, and

$$|K_2K| < |K_3K|$$

Therefore the denominator in the values of a is positive. Also we have $0 < a < 1$ at the minimum point

The second condition for the minimum is that at this value of a,

$$\frac{d^2\phi(a)}{da^2} > 0$$

Now

$$\frac{d^2\phi(a)}{da^2} = \frac{6K_1K}{a^4} - \frac{4K_1K}{a^3} + \frac{2K_2K}{a^3} + \frac{2K_3K}{a^3} - \frac{2K_1C_A}{a^3}$$

$$= \frac{1}{a^3}\left(\frac{6K_1K}{a} - 4K_1K + 2K_2K + 2K_3K - 2K_1C_A\right)$$

Substituting the value of a in the first term in the brackets, we have:

$$\frac{d^2\phi(a)}{da^2} = \frac{1}{a^3}(2K_1K - K_2K - K_3K + K_1C_A) > 0$$

Therefore there occurs a minimum at

$$a = \frac{2K_1K}{2K_1K - K_2K - K_3K + K_1C_A}$$

Let us now assume that the undissociated molecules of acetic acid do not act as a catalyst. We have then

$$K_{\text{homo.}} = K_2(C_A + aC) + K_3aC$$

$$= \frac{K_2[K(1 - a) - aC_A]}{a} + \frac{K_3[K(1 - a) - aC_A]}{a} + K_2C_A$$

$$= \frac{K_2K}{a} - K_2K + \frac{K_3K}{a} - K_3K - K_3C_A$$

If there is a minimum, then

$$\frac{dK_{\text{homo.}}}{da} = \frac{-K_2K}{a^2} - \frac{K_3K}{a^2} = 0$$

whence

$$K_2 = -K_3$$

That is, K_2 is equal to K_3, although opposite in sign. This is experimentally incorrect, for we find that $|K_3| > |K_2|$. Hence the undissociated molecules of acetic acid must act as a positive catalyst.

The results obtained by us show that reduction of silver ion by ferrous ion, in addition to being a heterogeneously autocatalyzed process wherein silver particles act as a heterogeneous autocatalyst, is also a homogeneously catalyzed reaction catalyzed by undissociated molecules of acetic acid and basic ions. Hydrogen or rather hydronium ions, H_3O^+, decrease the reaction velocity. A further discussion of these results will be published later, since these involve a revision of the present concepts of acids and bases as defined by Brønsted (1). Meanwhile the following remarks may be added:

1. According to Brønsted's concept of acid and base the primary condition for basic catalysis to occur is that the reactants must be able to transfer a proton

to the catalyzing base. In our case, the reactants are silver ion and ferrous ion and the question of the transfer of a proton does not arise.

2. Our conclusion—namely, that undissociated molecules of acetic acid act as a positive catalyst—is inconsistent with Brønsted's concept of general acid catalysis. Brønsted assumes that catalysis by an undissociated molecule of an acid is identical with catalysis by hydronium ions (H_3O^+) and that whenever acid catalysis occurs, it is to be ascribed quite generally to the molecules of the acid itself. We have shown that in our case the hydronium ion acts as a negative catalyst, while the undissociated molecule of acetic acid acts as a positive catalyst. In other words, in catalytic phenomena the undissociated molecules of an acid may behave differently from H_3O^+.

3. The authors feel that there is some fundamental relationship between oxidation–reduction on the one hand and acid–base catalysis on the other. There is some provision for such a relationship in Lewis' concept of acids and bases, according to which an acid is capable of accepting a share in a lone electron pair from a base, while a base donates a share in a lone electron pair to an acid. Accordingly an oxidizing agent may be regarded as an acid and a reducing agent as a base. But the analogy is only a formal one and can not be pushed to its logical conclusion. A detailed discussion can not be entered into here, but it appears that the formation of a covalent link is an essential intermediate step during oxidation–reduction reactions and from this point of view the occurrence of acid–base catalysis is apparent during oxidation–reduction reactions. This discussion will, however, be published later.

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