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Investigations on the Influence of Halogen and Sulfate Ions upon the Catalytic Activity of Silver

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It is shown in the present work that bromine ions (like chlorine ions) block up the active surface of the silver catalyst, in the decomposition of hydrogen peroxide. This process is connected with a specific adsorption, leading to an increase of the pH value of the medium. Owing to the decomposition of H_2O_2, which grows with the alkalinity of the medium, the curve: activity vs. conc. of Br^- passes through a maximum. The experimental data are in good agreement with Eq. (13), deduced for the above cases. Making an allowance for a Langmuir adsorption, the heat of adsorption of Br^- on silver has been calculated from the kinetic data as $\lambda^{a}_{Br^-} = 5060$ cal/mole. Analogous curves have been obtained for the effect of I^- and SO_4^{2-} ions upon the catalytic activity of silver in the decomposition of H_2O_2. The place of the maxima in the curves agrees with the theoretical assumption given.

INTRODUCTION

In an earlier publication (*1*) on the modification of silver-catalyst surface with chlorine ions it was shown that catalytic decomposition of hydrogen peroxide is connected with a specific adsorption process taking place:

$$2Ag + 2Cl^- + H_2O_2 = 2AgCl + 2OH^-$$

This results, on the one hand, in blocking up of the catalyst surface and on the other, in alkalization of the solution. Due to the first process, the active surface is diminished and as a result of the second, the decomposition of H_2O_2 is speeded up. Both effects, acting in opposite directions, determine the type of the modification curves, the latter passing through a maximum and asymptotically approaching a very small value with a high concentration of chlorine ions.

Modification curves of the same type should be expected with other modifiers also. Furthermore, the form and the place of the maxima will depend on the adsorption property of the modifying ion. A rough estimation of this property could be obtained by the Paneth-Fajance rule. It is of interest to make a comparative investigation on the influence of sulfate, chlorine, bromine, and iodine ions upon the catalytic activity of silver. A more detailed study was made on the influence of Br^-, while for the effect of the rest we obtained only preliminary results.

EXPERIMENTAL

The investigations were carried out by a method described in a previous work of ours (*1*).

The catalyst used was silver powder, the size of its particles, 0.15–0.25 mm. It was obtained by the thermal decomposition of pure Ag_2O at a temperature of 400°C. Hydrogen peroxide was first distilled in vacuum and then used in the form of a 0.6% solution. The reaction was carried out in an eudiometer. Mixing was accomplished with a shaker, while an ultrathermostat maintained a constant temperature. The quantity of catalyst taken for each experiment was 0.2000 ± 0.0002 g. The modifying ions were added to the solution in the form of potassium salts before adding the catalyst. The catalytic effect of the glass walls and that of the additives proved insignificant.

The oxygen liberated was measured at definite intervals in an eudiometer and the values recalculated for normal conditions. The experimental data obtained were in very good agreement with the kinetic equation for reactions of the first order which made the determination of the rate constant, *k*, possible.

RESULTS AND DISCUSSION

In all cases investigated it was found that the curves activity vs. added ions pass through a sharp maximum. The data obtained on the influence of Br^- upon the activity of silver at a number of different temperatures are shown in Fig. 1. Theoretically, this dependency could be treated in a way similar to the case of chlorine ions. We could assume the scheme of Roginski (*5*) (slightly modified), according to which there exist on the surface of the catalyst two kinds of sites active catalytically: donors and acceptors of electrons.

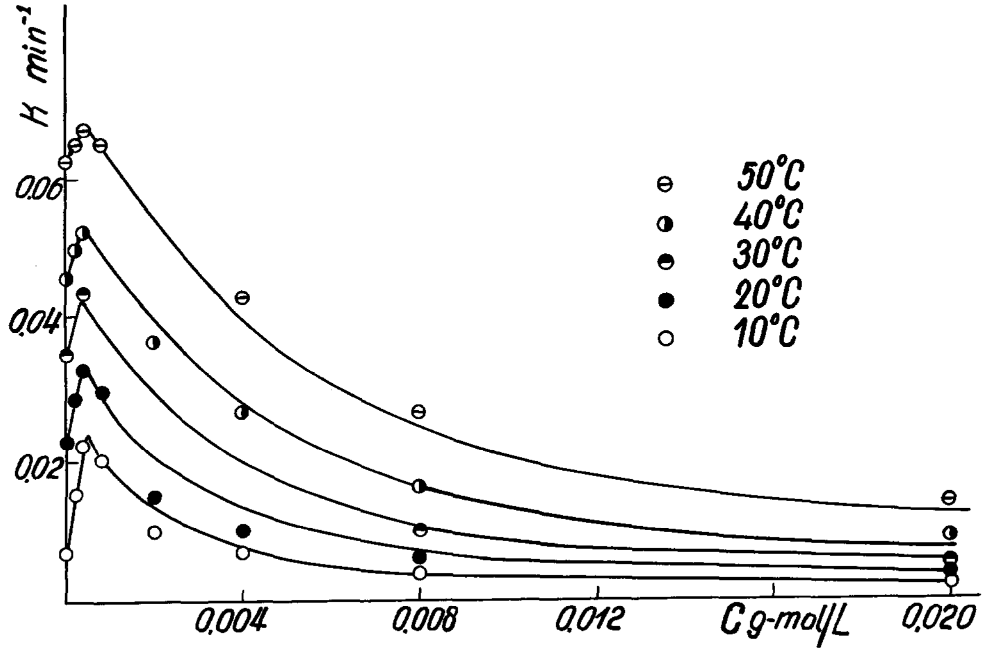

FIG. 1. Influence of concentration of Br^- on the activity of the silver catalyst at various temperatures; $C_{H_2O_2} = 0.6\%$.

Let us assume, moreover, that the adsorption of bromine ions on the donor sites makes transition of electrons from the surface of the catalyst to the peroxide easier. This assumption is made on the basis of electrochemical investigations. Frumkin (*6*) is of the opinion that halogen ions (for instance Cl^-) serve as bridges to facilitate transition of electrons toward the ion which is being neutralized. In a neutral or a slightly acid medium the rate of the following reaction:

$$H^+ + HO_2^- + e = OH^- + OH \quad \text{(on the donor site)} \qquad (1)$$

will be increased with the concentration of Br^- growing higher.

On the other hand, the acceptor sites will be blocked by the adsorbed Br^-, losing at the same time their activity with respect to the following reaction:

$$HO_2^- = HO_2 + e \quad \text{(on the acceptor site)} \qquad (2a)$$

$$O_2^{2-} = O_2 + 2e \qquad (2b)$$

The electrons liberated in the above reactions migrate toward the donor sites.

If we assume reaction (2a) to be the controlling stage of the above system of reactions, then

$$V = k^\circ C_{\mathrm{HO_2^-}} \quad (3)$$

Taking into consideration the dissociation of hydrogen peroxide:

$$V = k^\circ(K_c/C_{\mathrm{H^+}})C_{\mathrm{H_2O_2}} = k'C_{\mathrm{H_2O_2}} \quad (4)$$

Here K_C is the constant of the first stage of dissociation of H_2O_2. With $C_{\mathrm{H^+}} = \mathrm{const.}$, the reaction will be of the first order with respect to the concentration of hydrogen peroxide, as has been repeatedly confirmed by experiment.

If, however, in the presence of Br^- a quick adsorption process takes place:

$$\mathrm{Br^-} + \mathrm{Ag} = \mathrm{AgBr} + \mathrm{e} \quad (5)$$

the electrons liberated will take part in the reaction, additionally taking place on the donor sites, producing OH^-. This will result in the alkalization of the medium. The total concentration of OH^- in the solution will be:

$$C_{\mathrm{OH^-}} = C^\circ_{\mathrm{OH^-}} + (S/V)a_0\theta \quad (6)$$

where $C^\circ_{\mathrm{OH^-}}$ is the initial concentration of OH^- in the pure solution of H_2O_2, S is the surface of the catalyst, V is the volume of the solution, θ, the coverage of the active surface, and a_0, the maximum adsorption of Br^- on a unit surface. When the ion product constant of water is introduced, we obtain:

$$k' = k^\circ(K_c/K_w)[C^\circ_{\mathrm{OH^-}} + (S/V)a_0\theta] \quad (7)$$

or:

$$k' = k^\circ(K_c/K_w)C^\circ_{\mathrm{OH^-}}[1 + (Sa_0/VC^\circ_{\mathrm{OH^-}})\theta] \quad (8)$$

Let

$$k_n = k^\circ(K_c/K_w)C^\circ_{\mathrm{OH^-}} \quad (9)$$

and m

$$m = Sa_0/VC^\circ_{\mathrm{OH^-}} \quad (10)$$

Then

$$k' = k_n(1 + m\theta) \quad (11)$$

The expression thus obtained accounts for the change in the rate constant of reaction (2) only at the expense of the alkalization of the solution, due to adsorption process (5). As already assumed, however, the adsorption leads to a decrease of the number of active acceptor sites. In that case the rate constant of reaction (2) will be equal to:

$$k = k'(1 - \theta) = k_n(1 + m\theta)(1 - \theta) \quad (12)$$

or

$$k = k_n[1 + (m - 1)\theta - m\theta^2] \quad (13)$$

When the expression is differentiated with respect to θ, it will be found that

$$\theta_{\max} = (m - 1)/2m \quad (14)$$

and

$$k_{\max} = k_n[(m + 1)^2/4m] \quad (15)$$

If we assume that the adsorption follows a Langmuir isotherm:

$$\theta = C/(B + C) \quad (16)$$

the constant B for the different temperatures, for Br^- on the acceptor sites (hence, the heat of adsorption also) can be calculated from the data of the kinetic curves. It is quite sufficient to make use of the expressions for $\theta_{\max}$ and $k_{\max}$.

It is evident from Fig. 2 that lg B given as a function of $1/T$ represents a straight line. The heat of adsorption calculated is 5060 cal/mole.

In order to obtain the whole function $k = f(T,C)$ it is necessary to know the values of m at different temperatures. These values are directly furnished by the experiment, through $k_{\max}$. In this way were obtained the curves shown in Fig. 1. As is evident, the experimental data are in good agreement with the curves obtained theoretically.

The relationship between lg k and $1/T$ proved to be a straight line for the range of concentrations we worked within and that made the determination of the apparent energy of activation possible. It was found, as in the case with chlorine ions, that with the increase of concentration of bromine ions, the energy of activation first reaches a minimum (corresponding to the maxi-

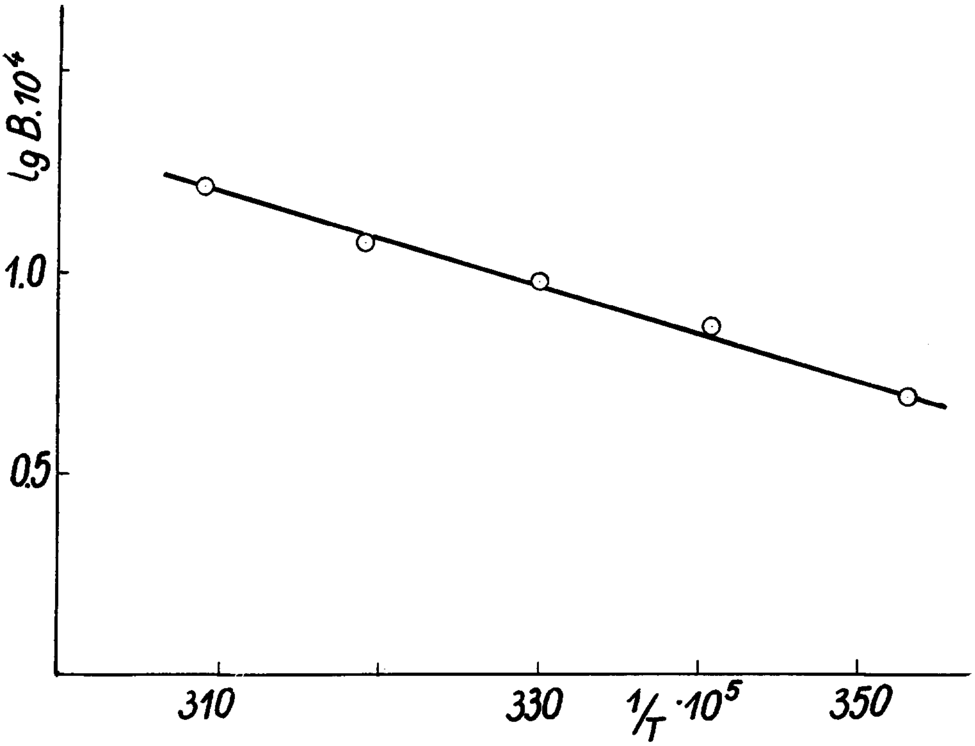

FIG. 2. Relationship between the logarithm of Langmuir's constant B and $1/T$.

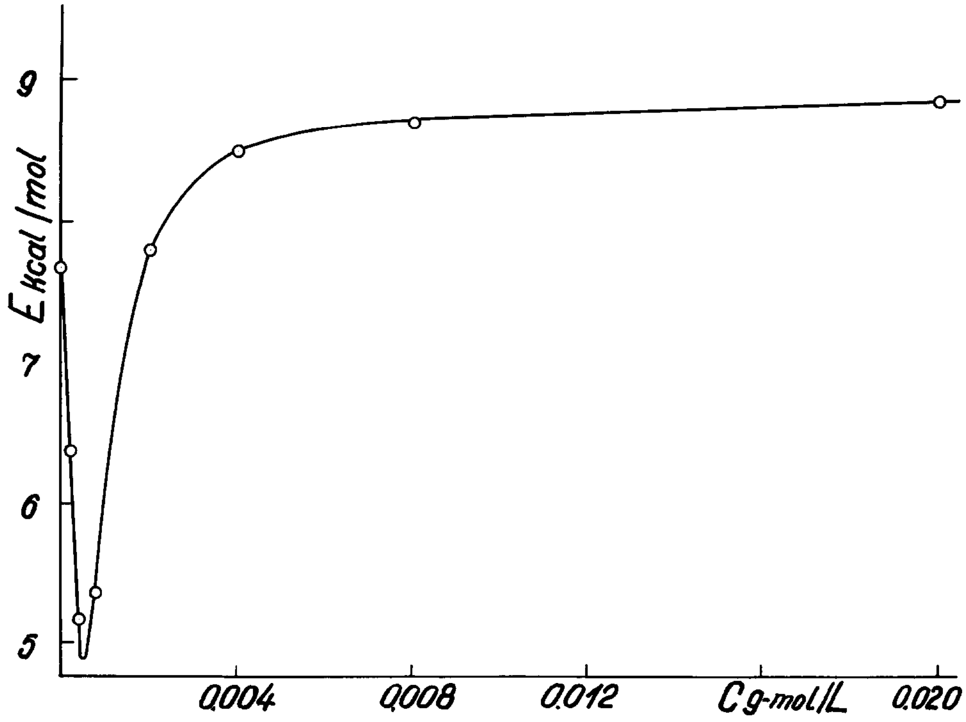

FIG. 3. Change of apparent activation energy of decomposition of H_2O_2 on Ag with concentration of Br^-; $C_{H_2O_2} = 0.6\%$.

mum in the curves) and then increases again (Fig. 3).

It should be noted that while the energy of activation in the process carried out on a nonmodified catalyst is lower than the energy of activation estimated by Bliznakov and Lazorov (*1*) under the same conditions, after passing through a minimum it approaches asymptotically 8800 cal/mole, as given in the work cited. The lower initial energy of activation could be explained by the difference between the properties of the silver powders used in the experiments. During the process of preparation, the silver powder could have retained some greater or smaller quantity of oxygen, which according to the investigations of Bliznakov and Peshev (*2*) leads to a change of its activity. Silver powder could, due to adsorption, also retain a certain (perhaps very small) quantity of KOH. The very slight alkalization of the solution which would accompany the application of such a catalyst would lead to a decrease of the apparent energy of activation. The fact that the curve approaches one and the same value of energy of activation, namely 8800 cal/mole, was to be expected. As was shown, this value is the energy of activation of the clean silver surface, i.e. of the rest of the not-yet-blocked acceptor sites.

The joint plotting of the relationship k/C for iodine, bromine, chlorine, and sulfate ions is given in Fig. 4. Apparently, in the series: sulfate, chlorine, bromine, iodine ions, the maxima of the modification curves are being shifted toward lower concentrations, becoming at the same time higher. The curve for iodine ions shows a constant activity, from concentrations higher than 8×10^{-4} g ion onward, which is due (with such concentrations of iodine ions) to a direct reaction taking place between hydrogen peroxide and the ions of iodine.

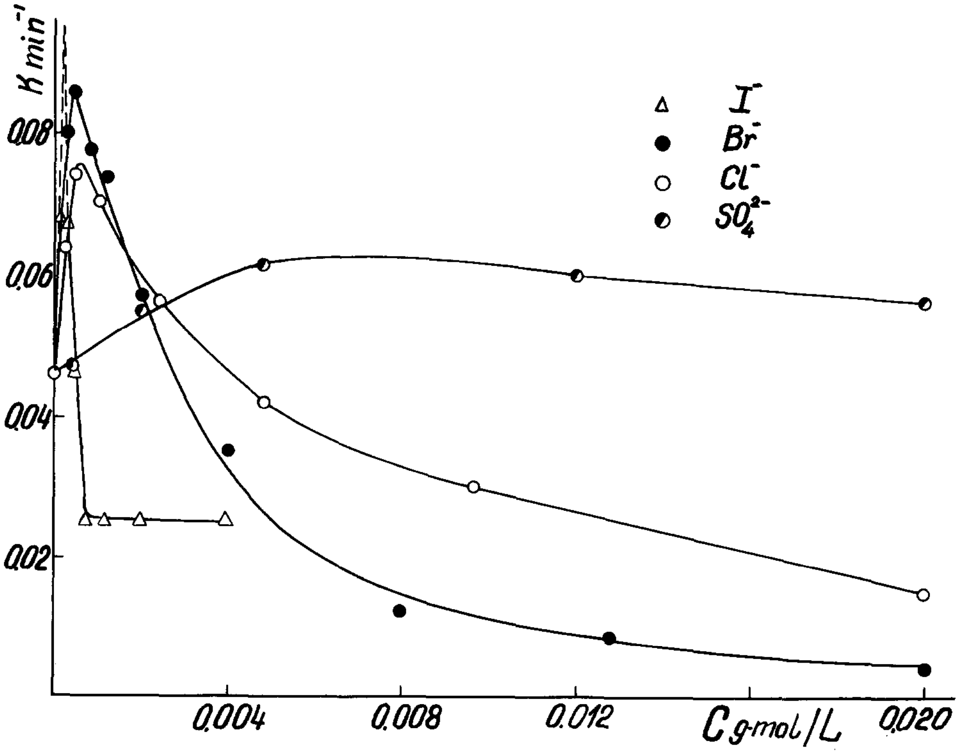

FIG. 4. Effect of various ions on the activity of silver in the decomposition of H_2O_2 at 25°C; $C_{H_2O_2} = 0.6\%$.

According to Eq. (13) the place of maximum should be determined by Eq. (14). With a Langmuir type of adsorption:

$$\frac{C_{\max}}{B + C_{\max}} = \frac{m - 1}{2m} \tag{17}$$

or

$$C_{\max} = B\left(1 - \frac{2}{m + 1}\right) \tag{18}$$

Therefore, the place of maximum will depend on the value of constant B (which on its part is a function of the heat of adsorption of a given kind of ions on the silver surface), as well as on the value of m. The latter is a constant, depending on the active surface of the catalyst used. As it was found (*3*) that this active surface is not a constant, due chiefly to the concurrent adsorption of hydroxyl ions (*4*), we could assume that constant m changes with respect to the modifying ion.

It was to be expected that along the series: sulfate, chlorine, bromine, iodine ions, the heat of adsorption would increase, as was confirmed by the experimental data obtained for chlorine (4360 cal/mole) and for bromine ions (5060 cal/mole). This leads to a diminution of the values of the corresponding constants along the same line.

The constant m will also increase along the above series, because that part of the active surface which is accessible to the modifying ion will also be increased in the same direction (*4*). Due to the relatively small changes of m, and to the comparatively quick changes of B, the influence of the latter will predominate. This means that along the series: sulfate, chlorine, bromine, iodine ions, the places of maxima in the k/C curves must be shifted toward lower concentrations. The experimental data shown in Fig. 4 are in good agreement with the above conclusions.

The values of the rate constant $k_{\max}$ at the points of maximum are given by Eq. (15). For the values of $m > 1$ [the constant m, in agreement with Eq. (14), can take no values smaller than 1], $k_{\max}$ is an increasing function of m. That is, in the series: sulfate, chlorine, bromine, iodine ions, along which the constant m increases, we should expect an increase also in the height of the maxima in the k/C curves. This conclusion too, is in good agreement with the experimental data.

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