JOURNAL OF CATALYSIS 25, 245-253 (1972)

On the Catalytic Activity of Silver

I. Activity, Poisoning, and Regeneration During the Decomposition of Hydrogen Peroxide

K. GOSZNER, D. KÖRNER, AND R. HITE

Physikalisch-Chemisches Institut der Universität München, Munich, Germany

Received August 24, 1971

The catalytic decomposition of hydrogen peroxide on silver has been studied with special reference to activity changes of the catalyst.

Initial-rate measurements confirm our previous results from concentration-change measurements. The reaction is of second order in 10–0.25 M solutions; in the range of lower concentrations it follows first order kinetics.

During the decomposition the catalytic activity of silver is reduced, depending on the solution concentration and various other experimental conditions. The poisoning is caused by a partly irreversible sorption of the reaction product oxygen; oxide layers are formed only in 5–2 M H_2O_2 solutions. The course of the poisoning was studied in some detail.

Decomposition and poisoning are scarcely at all influenced by the effects of metal dissolution by the reactants, by the surface changes or by the silver ions evolved.

INTRODUCTION

During heterogeneous catalytic processes the reaction solution as well as the reaction products may modify the catalyst surface chemically and physically. Therefore, it is essential to know whether such changes occur and how they influence the catalytic activity, in order to obtain meaningful results of the reaction kinetics.

With the decomposition of hydrogen peroxide on silver

$$2\,H_2O_2 \xrightarrow{Ag} 2\,H_2O + O_2 \qquad (1)$$

the dissolution of silver proves to be a side reaction (*1,2*). Metal dissolution and oxidation may considerably change the surface condition of the catalyst, and possibly influence the decomposition rate to some extent (*3*).

The oxidation of silver has recently been the subject of detailed investigations (*4–6*). Only one of the silver oxides, AgO_x (*7*), is formed in aqueous solutions of hydrogen peroxide. Its formation and its stability on pure silver surfaces is restricted to a concentration range from 2 to 5 M H_2O_2, here reducing the catalytic activity very much. In our previous work (*2*) we found by examining the catalyst surfaces by means of electron diffraction that in solutions of other concentrations none of the silver oxides was formed. Nevertheless, the reaction product oxygen is probably chemisorbed on the silver surfaces or even absorbed into the metal, thus reducing considerably the catalytic activity (*2,8–10*). A detailed kinetic study of this "poisoning effect" is the aim of the present paper.

First of all, it had to be confirmed that our kinetic results obtained earlier (*2*) with long time experiments, i.e., for obviously "poisoned" catalysts, are also valid for the high initial rate activities of "unpoisoned" catalysts. Then, the course of the activity changes during the reaction was studied for various experimental conditions. Finally, we tried to find a reliable method of catalyst reactivation; we could find it in a cathodic reduction treatment which permits a regeneration with nearly quantitative reproducibility.

In order to obtain reliable and comparable results, the catalyst samples were always carefully pretreated by the same procedure (polishing and etching). The influence of different pretreatments on the catalytic activity will be reported in a following Part II.

METHODS

Materials

Decomposition kinetics are strongly influenced by trace impurities in the reaction solution or at the catalyst surface (11). Hence, the use of high purity reagents as well as extreme care in preparing the catalysts are essential.

The hydrogen peroxide used was produced electrochemically from inorganic materials and kindly supplied by Elektrochemische Werke München. Samples of this unstabilized H_2O_2 (ca. 70 w/w) were twice distilled under vacuum at 50°C (*11*) and then diluted with triply distilled water.

Catalysts were taken from a silver sheet of 99.999% purity (Degussa). Clean surfaces for the kinetic experiments were prepared by polishing with fine-grade emery paper and etching for 30 sec in 50% HNO_3, followed by a 30 min rinse in 25% H_2SO_4. After each procedure the catalysts were thoroughly rinsed with triply distilled water.

Rate Measurements

The reaction kinetics were studied in a closed system by measuring the rates of oxygen evolution.

A three-neck flask (Solidex), containing the H_2O_2 solution, was connected with a soap-film flow meter. The reaction temperature was controlled by a thermostat bath to ± 0.2°C. Two devices were used to provide stirring and to hold the silver catalyst: (i) The silver sheet was wedged between the disks of a Teflon spindle which was attached at the stirring axis; (ii) in order to facilitate the exchange of the catalyst samples and to make more definite the starting times of the reaction runs, the silver sheet was suspended on a glass hook, and stirring was provided by a glass paddle. It was assured by several tests that neither for these different devices nor for different stirring velocities did any changes in reaction rate result.

Before each experiment, the reaction flask, the stirring device, and the catalyst support were carefully cleaned by degreasing in hot 10% NaOH, rinsing with conc. HNO_3 and twice leaching from adsorbed ions in boiling triply distilled water. In the cleaned apparatus there was no detectable decomposition of H_2O_2 on the glass or teflon surfaces.

Before starting a decomposition run, the initial concentration c_0 of H_2O_2 was determined by titration of acidified solution samples with $0.1\,M$ $KMnO_4$. Some intermediate titrations and that of the final concentration after each run served to check the accuracy of the indirect evaluation of the concentration changes by numerical integration for the oxygen evolution measurements.

Experimental data were plotted as log $(R_\tau V/S)$ vs log c_τ (see Figs. 1–3), where R_τ and c_τ are the reaction rate and peroxide concentration at time τ, V is the volume of the reaction solution, and S the (geometric) surface of the catalyst. From such plots the experimental reaction orders n and rate constants k_n were obtained, corresponding to the simple rate equations for heterogeneous reactions

$$R = (k_n S/V)\, c^n \quad \text{(moles decomposed/liter min)}.$$

RESULTS

Rates and Reaction Orders

Previous experiments (*2*) have shown that in solutions with $c > 0.25\,M$ the decomposition of hydrogen peroxide on silver is a second order reaction and in less concentrated solutions a first order reaction (*2,8*). We obtained those results by titration determinations of the hydrogen peroxide concentrations. Measuring now the rates of oxygen evolution, it has become possible to obtain better "initial rate" values and to follow the course of the reaction almost continuously.

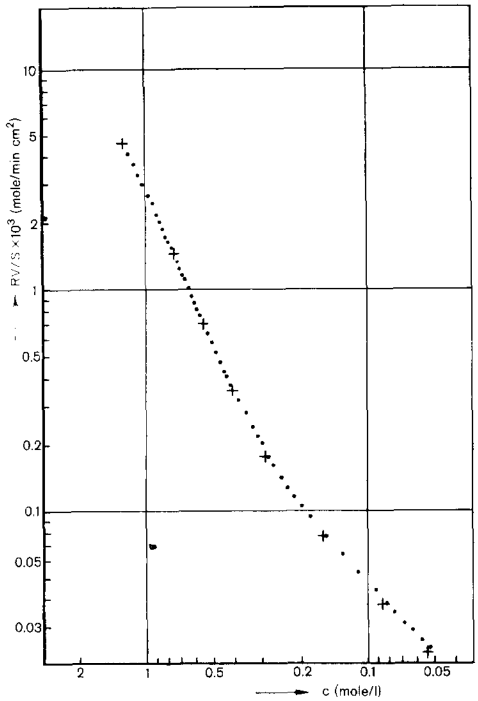

FIG. 1. Decomposition rate of H_2O_2 vs H_2O_2 concentration at 35°C. Concentration values: (●) calculated from rate measurements, (+) determined by titration.

Concentration-change runs. Figure 1 shows the decrease of the decomposition rate during 4.3 hr, when the concentration of the solution decreases from 1.25 to 0.05 *M*. The rates of O_2 evolution were measured at intervals of 0.5 min at high rates to 5.0 min at low rates.

In the course of such experiments the pH rises slightly (in pure solutions from about 5.5 to 6.5) with decreasing H_2O_2 concentration, according to the equilibrium condition

$$\frac{(H^+)(OOH^-)}{(H_2O_2)} = K_{H_2O_2}$$
$$= 3.5 \times 10^{-12} \text{ mol/l (at 35°C)}.$$

This change does not affect the reaction rate in acid, neutral, and slightly alkaline solution (*1,2*). Between 1.25 and 0.4 *M* H_2O_2 the slope of the curve in Fig. 1 is $n = 2.3$; then it decreases to the final value $n = 1.1$ at low concentrations.

Initial-rate measurements. The initial decomposition rates which were measured about 0.5 min after starting the reaction with freshly prepared catalysts and renewed solutions for different concentrations, however, fit straight lines with $n = 2.0$ or $n = 1.0$, respectively (Fig. 2).

Silver sheets with different areas were used and the solution volumes varied from 0.150 to 0.498 liter. It is remarkable how slightly the initial rate values deviate from the straight lines, representing the second and first reaction order.

As far as the single experiments after the measurement of the initial rates were continued, they also revealed a decline of the decomposition rates with $n > 2$ or > 1, respectively; this became more evident by using catalysts of smaller surface areas. From this it may be concluded that the respective values, $n > 2$ or > 1, represent apparent reaction orders only, arising from

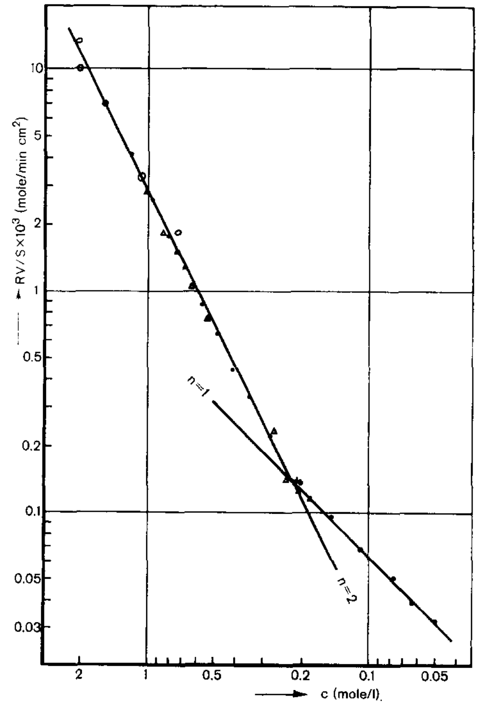

FIG. 2. Initial rates vs H_2O_2 concentration at 35°C for silver sheet catalysts of different areas; straight lines represent a second and a first order, respectively. Catalyst areas (in cm²): ○—1.46, △—3.78, ●—4.46, +—8.10.

the simultaneous deactivation (poisoning) effect during the course of decomposition.

Concentrated solutions (10 to 2 *M*). Measurements in the range of more concentrated solutions have been of some interest for two reasons. As mentioned before, an oxide layer is formed on the silver surface in solutions from 2 to 5 *M* H_2O_2 (*2,7*); this should become apparent also in the initial-rate measurements. Furthermore, in highly concentrated solutions Baumgartner *et al.* (*1*) found the decomposition reaction to be of first order; therefore we wondered if such a transition from the first to second order would also appear in our experiments.

The results of the experiments with 10 to 1 *M* solutions are shown in Fig. 3. In all measurements the reaction solutions had the same volumes (0.098 l). Small silver wires (area = 0.157 cm^2), freshly etched before each experiment were used as catalysts. Each run was followed for about 30 min. In the diagram the highest values for the reaction rates are mean values of two measurements taken during the first 30 sec of the reaction time. The following values correspond to about 30, 45, and 60 sec reaction times.* The large differences between these first values show a rapid drop of the reaction rates at the beginning of the runs, especially for more concentrated H_2O_2 solutions. Later on the rates decrease more slowly; finally some curves show a tendency towards a stationary reaction course.

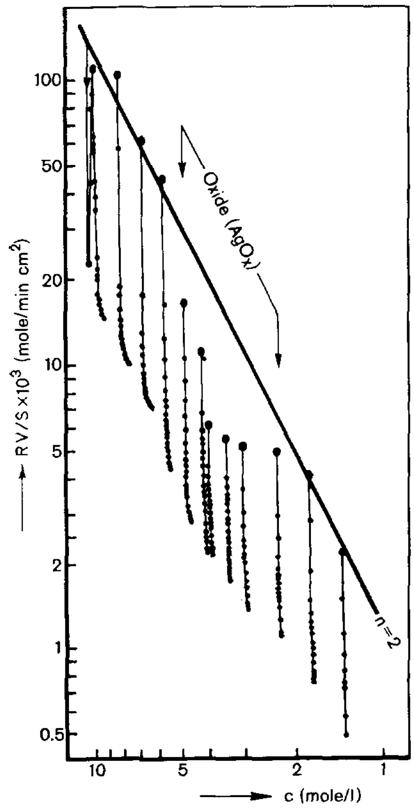

FIG. 3. Initial rates (big dots) and poisoning in concentrated solutions at 20°C, with a straight line representing the second reaction order.

Evidently, the maximum values of these experiments are not real initial rates. Nevertheless, the straight line in Fig. 3, representing a second order reaction, comprises quite well the maximum rates of the experiments with c_0 = 10.45, 8.39, 6.90, and 5.80 *M* H_2O_2, and also those with c_0 = 1.80 and 1.38 *M* H_2O_2. A transition to a first order reaction is not found in this concentration range. The lower rates with c_0 = 4.94, 4.26, 4.07, 3.52, 3.06, and 2.35 *M* are due to the formation of AgO_x layers. It should be pointed out once more that apart from this concentration range no stable oxide layers are formed, not even after long reaction times (cf. (*2*)).

The Rate Constants

With the results plotted in Fig. 3 for the experiments with concentrated solutions, small solution volumes, and catalysts of small surface areas, the poisoning effect has become very obvious. The impairment of catalyst activity also in solutions with concentrations below 1 *M* will be shown now by studying the changes of the rate "constants" in the course of the reaction. Hereby, remarkable differences are revealed for different experimental conditions.

In order to obtain the activity changes we assumed (cf. above) the reaction orders to have the constant values n = 2.0 or

---

* The reaction starting at 10.45 *M* H_2O_2 had an irregular initial period; a regular course followed the maximum after 90 sec reaction time.

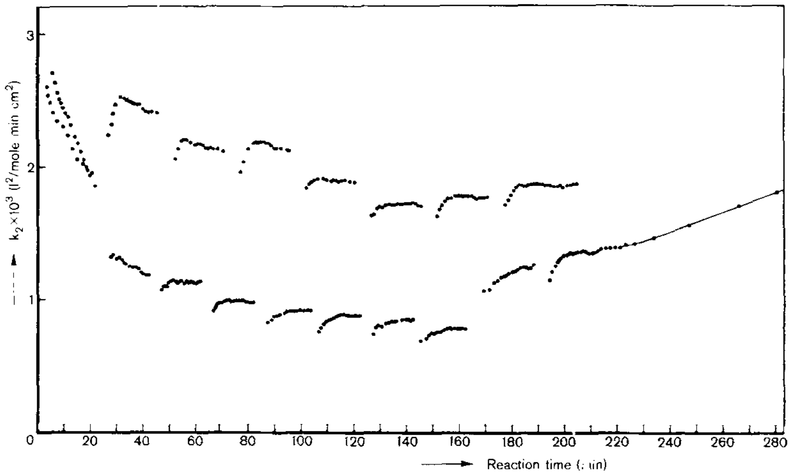

FIG. 4. Catalyst poisoning in "repeated runs" (renewed solutions) and "subsequent runs" (reconcentrated solutions) at 35°C, pH ≈ 5.5.

$n = 1.0$ during a run, and we accordingly calculated rate constants for each single rate measurement from

$$k_2 = VR_\tau/Sc_\tau^2 \text{ (liters}^2\text{/mole min·cm}^2\text{)}$$
$$k_1 = VR_\tau/Sc_\tau \text{ (liters/min·cm}^2\text{)}$$

respectively. These values are plotted vs reaction time τ in Figs. 4 and 5.

Second-order range. (a) Primary runs. The left part of Fig. 4 shows the reaction course with a catalyst pretreated as usual: k_2 steadily decreases to ⅔ of its initial value during the reaction time of 21 min.

(b) Repeated runs. For each of the following experiments (upper drawings in Fig. 4) the solution was renewed, but the catalyst only rinsed with triply distilled water and used again without further treatment. All these *"repeated runs"* show the same course: k_2 increases for a short time which may be interpreted as a partial depoisoning of the catalyst, followed again by a gradual poisoning. Altogether the

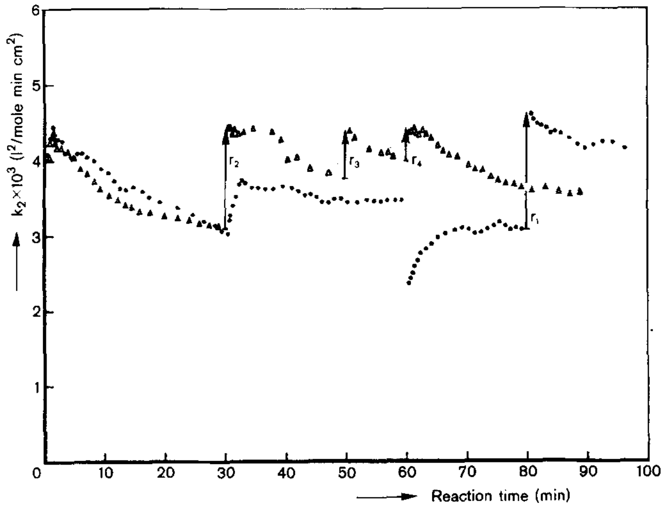

FIG. 5. Poisoning in "repeated runs" with slightly alkaline solutions (pH ≈ 8.5) at 35°C. Reactivation by cathodic reductions (r_1, r_2, r_3, r_4).

rate constant slowly approaches a stationary value at about ⅔ of the initial value of the primary run. In these experiments the initial concentration was always $c_0 = 0.98\,M$, and the final one 0.54 to $0.46\,M$ after 20 min reaction time.

(c) Subsequent runs. In another series of experiments (lower drawings in Fig. 4) the solution was not renewed but only brought to the initial concentration by adding some drops of (distilled) concentrated hydrogen peroxide. In such "*subsequent runs*" the rate constant further decreases: on an average the k_2 values are half as high as the corresponding values of the repeated runs. After the seventh subsequent run the solution was renewed: the reaction proceeds with higher and increasing rate constants but the k_2 values approach the level of the upper curves only slowly (after a second renewal of the solution).

(d) From the difference between repeated and subsequent runs it becomes evident that the poisoning can hardly be caused by impurities from the solution (which would imply an additive effect), but that the poisoning is apparently stronger when the solution is not renewed, or alternatively when the catalyst is not removed from the reaction solution. Thus, the catalyst presumably becomes poisoned partly irreversibly by a reaction product. This can also be proved simply by enlarging the solution volume. After diluting with triply distilled water or after addition of equally concentrated hydrogen peroxide solution, the system is only slowly reactivated to some extent.

First-order range. In series of experiments with solutions of lower concentration ($c_0 = 0.25\,M$, final concentration 0.20–$0.18\,M$ after 30 min reaction time) we obtained corresponding results, but with a smaller degree of poisoning. During the primary run k_1 decreases from 0.65 to 0.54×10^{-3} 1/min cm^2. In seven *repeated runs* (30 min each) no further poisoning occurs. Each of these runs shows the same course as described before: a short increase of k_1 from 0.56 to 0.59×10^{-3} 1/min cm^2, followed again by a gradual decrease to 0.54×10^{-3} 1/min cm^2. In *subsequent runs* a depoisoning period scarcely occurs, and k_1 further decreases on an average of 2% from run to run.

Influence of silver dissolution. Alkaline solutions. In a solution of $1\,M$ H_2O_2 (pH $\simeq 5.5$) about 0.1 mg of silver is dissolved from 1 cm^2 catalyst surface in one hour (*2,3*). In order to see to what extent the silver ions may contribute to the poisoning of the reaction system, small amounts of a solution of silver sulfate were gradually added to the reaction solution: 60 mg of dissolved Ag_2SO_4 are necessary to reduce the reaction rate by 10%; the addition of 600 mg lowers the rate by about 20%. These values prove that the poisoning by the silver ions dissolved from the catalyst surface during the reaction may be neglected in our experiments.

To eliminate the dissolution of silver and the surface changes eventually caused thereby, measurements were also made with slightly alkaline solutions (pH $\simeq$ 8.5). No dissolution of silver occurs here (*2*). Nevertheless, the same decrease of k_2 is found during the reaction (see lower drawings with circled points in Fig. 5). The relative decrease of k_2 as well as the partial depoisoning in renewed solutions quantitatively agree with the values measured in pure H_2O_2 solutions (pH $\simeq 5.5$, cf. Fig. 4). The absolute values of k_2 are somewhat higher, since the decomposition kinetic becomes already dependent on pH in this range (*2*).

The Regeneration of the Catalysts

In the course of the second repeated run in Fig. 5, after a total reaction time of 80 min, we tried to regenerate the catalytic activity of the silver by a cathodic reduction.* After this treatment (marked by r_1 in Fig. 5) the decomposition reaction in the non-renewed solution proceeds with a

---

* Cathodic reduction in $1\,M$ H_2SO_4 at 6 V, current about 600 mA at a catalyst area of 5.95 cm^2. Reduction time in these experiments 1 minute. Varying the reduction time from 5 to 160 sec does not yield any change of the results. Further details will be given in Part II of our studies.

reaction rate equivalent to the maximum value of the primary run.

A second series of experiments with a primary and two repeated runs (drawn with triangles in Fig. 5) confirms that it is possible to regenerate the catalytic activity of the silver quantitatively by cathodic reductions (r_2, r_3, r_4). It has been proved that a mere treatment in dilute sulfuric acid (dissolution of oxide) does not regenerate the catalyst activity.

The accuracy of our results in general can be seen from Fig. 1–5: With carefully prepared doubly distilled solutions of hydrogen peroxide a regular course of the decomposition reaction on silver is obtained (Fig. 1). The reaction courses are reproducible within 10% (Fig. 2, 4, and 5). The reproducibility of measurements after cathodic regeneration is nearly quantitative. Irregularities sometimes occur at the very beginning of the reaction, (e.g., the first measurements in Figs. 3 and 5), probably caused by trace impurities on the silver surfaces. In such cases, the catalyst activity reaches a maximum after one or two minutes, then the reaction proceeds as usual. During a run the measured values do not fluctuate more than 1%; this fluctuation mainly originates from errors in time measuring.

Discussion

1. In previous studies (*2*) it has been stated that the kinetics of hydrogen peroxide decomposition on silver obey simple laws with integral reaction orders $n = 2$ or $n = 1$, respectively. These results were obtained from concentration-change (long time) runs with catalyst samples already in a stationary state of activity. Now they could be confirmed for the highly active, unpoisoned state of freshly prepared catalysts by means of initial rate measurements: The reaction takes a first order course in less concentrated solutions ($c < 0.25\,M$ H_2O_2); above $c = 0.3\,M$ it follows a second-order law. Even up to $c = 10\,M$ no change occurs, though for highly concentrated solutions also first order kinetics have been reported (*1*).

It may be concluded from these results that the kinetics follow true integral orders in every case, whether the catalysts are poisoned or not. Concerning the deviations, the higher apparent orders found sometimes (Fig. 1, $n > 2$ or $n > 1$) result rather from measuring a decomposition which is accompanied simultaneously by a deactivation conditioning (*Formierung*) of the catalyst to a stationary activity. Thus, the poisoning probably does not influence the reaction mechanism but the reaction dynamics only, characterized by the frequency factor and activation energy (available active sites, modification of the electronic factor of the catalyst).

In the range of the second order kinetics an activation energy of 10 kcal/mol and a frequency factor of 10^4 liter^2/mol min cm^2 was found (*2,20*). These values were measured in long time runs, therefore they are only valid for "poisoned" catalysts in a stationary state of activity. At that time we discussed a molecular mechanism (*20*) with an intermediate oxidation of the silver catalyst, which describes the first order reaction in very high and in very low concentrated solutions as well as the second order reaction between. This mechanism will be discussed again as soon as the changes of the activation energy and of the frequency factor are studied with the same accuracy as the changes of the rate constant.

2. In the present experiments we could exclude a poisoning by *trace impurities* (by use of doubly distilled H_2O_2, triply distilled water, carefully prepared catalysts, and avoiding any use of tap grease, etc). Moreover, it has been shown once more that the *silver ions* dissolved from the catalyst surface during the reaction do not noticeably affect the decomposition reaction. The same seems to be valid as regards *changes of the surface structure* due to this etching effect of the reactant. Besides, in experiments with slightly alkaline solutions an etching and surface change was avoided completely.

The formation of a stable *oxide layer* (AgO_x) is restricted to the concentration range from 2 to $5\,M$ H_2O_2, as can be seen from Fig. 3 (cf. also *2,7*). Thus, oxide formation is to be excluded as a poisoning source also here.

3. Nevertheless, a poisoning does occur during the decomposition reaction, and the reaction product oxygen presumably causes this in all concentration ranges either by chemisorption or absorption in a boundary layer.

The poisoning takes a faster course in more concentrated solutions, due to the more violent oxygen evolution; it apparently depends on the surface area of the catalyst and on the quantity of the reaction solution. By renewing the solution, it is possible to regenerate the reaction system, but only slowly and not completely. Hence it follows that the interaction of oxygen is partly irreversible.

Summarizing, we come to the following conclusions on the poisoning effect:

(I) It must be due to adsorption (or absorption) of an agent which originates from H_2O_2 decomposition, and which is dissolved in the reaction solution with an increasing concentration (c_p) during the decomposition experiments. The higher the concentration of poison c_p, the higher is θ_p, the fraction of surface covered with it, in accordance with the different poisoning phenomena:

(a) *Increase of poisoning with time:* increase of c_p, which is small in a new solution (c_{po}).

(b) *Repeated runs; dilution* with triply distilled H_2O; *addition* of new H_2O_2 solution (depoisoning): diminution of $c_p \rightarrow c_{po}$.

(c) *Subsequent runs:* no remarkable change of c_p due to addition of small portions of conc. H_2O_2. Thus, in contrast to (*b*), poisoning continues.

(d) *Use of small solution volumes* (marked poisoning): Less time is necessary to obtain a certain c_p by decomposition.

(II) As regards the poisoning agent, there can be excluded:

(a) *Foreign substances:* because of I(b).

(b) $OH_{ad} \rightleftarrows OH$ *or* OH^-*:* OH is a carrier of decomposition in the case of a chain mechanism; furthermore, it is not stable in bulk solution. OH^-: there is no increase of poisoning with pH. The same or similar holds for OOH, OOH^-.

Thus, there seems to remain only O_2 adsorption (product poisoning*) or absorption, whereby the solutions used in H_2O_2 decomposition gain an increased O_2 concentration in comparison with "normal" or "new" solutions.

It is well known from gaseous reactions on silver catalysts that oxygen is chemisorbed irreversibly to some extent either as molecules (*12,13*) or as atoms (*14,15*). Moreover, considering the results of several investigations on the anodic oxidation of silver (*4,6,9*), or the decomposition of H_2O_2 on silver and silver alloys (*9*), it seems likely that atomic oxygen diffuses into the surface layers of the silver lattice. This implies a change of the electronic structure of silver, by which the decrease of its catalytic activity during the decomposition reaction can be explained (*9*). Bliznakov and Peschev (*8*) also concluded from experiments with silver plates, heated in air or vacuum, respectively, that the catalytic activity changes due to oxygen being chemisorbed on the silver surface. A recently published investigation of Bliznakov and Lazarov (*10*) seems to confirm this, also pointing out the significance of the electronic factor for the catalytic properties of the group Ib-metals.

With catalysts pretreated under vacuum, these authors found a lingered start of the reaction ("latent period"). They concluded that the chemisorption of oxygen is necessary to build up the catalytic activity of silver. These experiments were carried out with extremely dilute solutions ($c = 0.02\,M$ H_2O_2) at low temperatures; in our experiments ($c > 0.05\,M$, $T = 35°C$) the small amount of oxygen necessary to activate the catalyst, was obviously chemisorbed "at once." Though our measurements began not later than 0.2 min after the start of the decomposition, the reaction was already in that range where a further adsorption deactivates the silver (cf. (*8*)). Even with catalysts heated in argon for several hours

---

* A product poisoning by oxygen occurs also in the decomposition of N_2O on Ag, for which system the rate law is $k(N_2O)/(1 + k'(O_2))$, (whereas for Au the rate is not influenced by oxygen!).

no starting period could be observed (cf. Part II, to be published). Experiments with an addition of oxygen to the system showed no detectable effect. Nevertheless, the ability of silver to chemisorb oxygen (perhaps dissociatively) is likely to be the presupposition of its high catalytic activity for the decomposition of hydrogen peroxide, and the formation of an intermediate oxidation stage has been postulated in order to explain several gas reactions on silver (cf. e.g., *16–19*).

The conclusions concerning the poisoning by oxygen are supported by the regeneration experiments with cathodic treatment of the catalysts. With this, moreover, a method of catalyst regeneration could be developed which warrants reliable and quite reproducible measurements of the reaction.

ACKNOWLEDGMENTS

The authors wish to thank Professor Dr. G.-M. Schwab for his continued interest during this work. Thanks are also due to the Deutsche Forschungsgemeinschaft and to the Fonds der Chemischen Industrie for financial aid.

REFERENCES

1. BAUMGARTNER, H. J., HOOD, G. C., MONGER, J. M., ROBERTS, R. M., AND SANBORN, C. E., *J. Catal.* **2,** 405, 415 (1963).

2. GOSZNER, K., HEIDRICH, H., AND KÖRNER, D., *Z. Phys. Chem. N. F.* **67,** 220 (1969); **68,** 293 (1969).

3. MAGGS, F. T., AND SUTTON, D., *Trans. Faraday Soc.* **54,** 1861 (1958); **55,** 974 (1959).

4. FLEISCHMANN, M., *Trans. Faraday Soc.* **64,** 3120, 3128, 3137 (1968). BRIGGS, G. W. D., FLEISCHMANN, M., LAX, D. F., AND THIRSK, H. R. *Trans. Faraday Soc.* **64,** 3120 (1968). FLEISCHMANN, M., LAX, D. F., AND THIRSK, H. R., *ibid.* **64,** 3728, 3737 (1968).

5. GOSZNER, K., EFTYCHIADIS, T., AND KÖRNER, D., *Naturwissenschaften* **56,** 137 (1969).

6. GOSZNER, K., EFTYCHIADIS, T., AND KÖRNER, D., *Z. Naturforschung* **24a,** 807, 813 (1969).

7. GOSZNER, K., AND POLLE, H., *Z. Phys. Chem. N. F.* **54,** 93 (1967).

8. BLIZNAKOV, G., AND PESCHEV, O., *Naturwissenschaften* **48,** 551 (1961).

9. POLLE, H., Thesis, University of Munich, 1965.

10. BLIZNAKOV, G., AND LAZAROV, D., *J. Catal.* **14,** 187 (1969).

11. GOSZNER, K., HITE, R., AND KÖRNER, D., *Z. Phys. Chem. N. F.* **74,** 67 (1971).

12. DE BOER, J. H., *in* "Advances in Catalysis" (W. G. Frankenburg, V. I. Komarewsky, and E. K. Rideal, eds.), Vol. 9, p. 472. Academic Press, New York, 1957.

13. THOMAS, J. M., AND THOMAS, W. J., "Introduction to the Principles of Heterogeneous Catalysis," p. 31. Academic Press, London, 1967.

14. GRIFFITH, R. H., AND MARSH, J. D. F., "Contact Catalysis," p. 83. Oxford Univ., New York, 1957.

15. RIDEAL, E. K., "Concepts in Catalysis," p. 27. Academic Press, London, 1968.

16. DEBOER, J. H., *in* "Advances in Catalysis" (D. D. Eley, ed.), Vol. 8, p. 17. Academic Press, New York, 1956.

17. BOND, G. C., "Catalysis by Metals," p. 452. Academic Press, London, 1962.

18. FELLER-KNIEPMEIER, M., FELLER, H. G., AND TITZENTHALER, E., *Ber. Bunsenges. Phys. Chem.* **71,** 606 (1967).

19. SCHWAB, G.-M., AND GOSZNER, K., *Annu. Rev. Phys. Chem.* **14,** 177 (1963).

20. HEIDRICH, H. Thesis, Universität München, 1966.