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The Silver-Catalyzed Homomolecular Oxygen Exchange Reaction*

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The silver-catalyzed homomolecular exchange reaction between oxygen-16 and oxygen-18 has been studied in the 500–700°C temperature range. In the presence of silver wire between 500° and 575°, the activation energy is 29.4 kcal/mole and the order of the reaction with respect to oxygen is 0.52. At 650°, the order of the reaction with respect to the oxygen pressure decreases to 0.20 and the activation energy for the process is only 16.5 kcal/mole. The effect of the silver catalyst on the heterogeneous exchange between oxygen gas and sodium molybdate, sodium chromate, and potassium sulfate was also studied and these results are compared with those in the absence of the catalyst. A comparison of the activity of silver with that of the other noble metals as catalysts for the oxygen exchange reaction is made.

INTRODUCTION

The adsorption of oxygen on silver has been investigated extensively by many workers (*1–4*). Additional investigations were undertaken in an attempt to explain the exceptional activity of silver as compared with the other noble metals such as gold, platinum, and palladium in the catalysis of the low-temperature oxidation of hydrocarbons (*5*). The formation of atomic species, relatively stable oxides or peroxides, and mobile molecular species such as O_2^{2-} and O_2^- have been considered, but the state of oxygen on the surface is still not clearly understood.

The homomolecular isotopic exchange or the scrambling reaction oxygen molecules appears to require chemisorption of oxygen regardless of the reaction mechanism involved (*6, 7, 8*). Therefore, a study of the kinetics of oxygen exchange on a silver surface was undertaken to see if it gives detailed information about the nature of the adsorption process. This approach is particularly useful when the adsorption of gas is small and the conventional gas-uptake and calorimetric methods are difficult to apply.

Margolis (*6*) has studied the homomolecular oxygen isotopic exchange reaction on silver in the temperature range between 200° and 320°C. The rate of exchange was found to be smaller than the rate of adsorption at low temperatures and much smaller than the rate of catalytic oxidation of ethylene on silver. It was concluded that the oxygen is only partially dissociated on silver and the catalytic oxidation proceeds primarily by the formation of a molecular oxygen ion, O_2^-.

In this paper, we wish to report the details of the homomolecular oxygen exchange reaction on silver in the 500–700°C temperature range. In the course of this study, it was found that silver measurably catalyzed the heterogeneous exchange reaction between gaseous oxygen and the glass vessel in which the homomolecular exchange was studied. Owing to the importance of this heterogeneous catalysis in the evaluation of the nature of the chemisorption process

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of oxygen on silver, we also investigated the influence of silver on a number of heterogeneous exchange reactions between oxygen gas and some oxides and inorganic salts on which data are available for comparison.

EXPERIMENTAL

The oxygen exchange process was studied in a static system. A Vycor reaction vessel with a total of 90 ml was designed to allow the periodic withdrawal of small samples of oxygen gas for isotopic analysis with RMS-11, a Nuclide Analysis Associates Mass Spectrometer.

The vessel itself was similar in design to that used by Shakhashiri and Gordon (*9*). The sampling port was located immediately above the silver wire which was suspended in the vessel itself. The technique employed for studying the isotopic exchange between gaseous O_2 and the various salts consisted of placing a 30–50 mg sample of the salt in a Vycor or quartz tube contained in a small furnace. For the series of silver-catalyzed solid reactions, wire with a total surface area of 5 cm^2 was suspended 1–2 cm above the solid sample. The sampling port was immediately above the silver wire. The progress of the reaction was monitored mass spectrometrically by periodically measuring the change in isotopic composition. Separate experiments over the temperature range studied showed that the overall reaction rates (and the internal precision of each experiment) were unaffected by periodic mixing via an external Toepler pump, which suggests that effects noted (*vide infra*) cannot be due to mixing or diffusion-controlled limitations.

Weighed amounts of the catalyst, in the form of silver wire or powder were placed in the reaction vessel and treated for 2 hr at 750° and a residual pressure of 10^{-4} torr. Considerable care was taken to clean the silver surfaces prior to each experiment. Pretreatment with hydrogen, although desirable to ensure removal of some types of impurities was not possible in that some hydrogen is retained by the metal and the surface properties would appear to be modified (*10*). The effects of various impurities, including other noble metals, the halogens, and hydrogen on the activity of the silver catalyst will be published at a later date. After the pretreatment, the temperature was lowered to the desired reaction temperature and the nonequilibrium mixture of oxygen gas was introduced into the reaction vessel. To avoid complications due to the simultaneous isotopic exchange between the gas and the reaction vessel during the course of the homomolecular oxygen exchange reaction, the vessel was preheated with oxygen gas of the original concentration of the heavy isotope until no further change in isotopic composition was observed. In the mass spectrometric analysis of the oxygen gas, the concentration of all the isotopic oxygen species with the exception of O^{17}–O^{17} was determined. The accuracy of any individual measurement was better than ±1%. The reaction vessel was heated by a thermostated resistance furnace with temperature control of better than ±1° at 700°C (*9*).

The oxygen-18–enriched oxygen gas was prepared by the electrolysis of enriched water obtained from YEDA (Israel). Nonequilibrium isotopic mixtures of oxygen gas were prepared from normal and 150 times enriched gas in the ratio of 1:5. The silver wire (99.99%) was supplied by the Johnson Matthey Co., Ltd. The silver powder had a nominal purity of 99.97% and was obtained from Fisher Co. The other chemicals were of C. P. grade.

RESULTS

Preliminary Experiments

A series of preliminary experiments was carried out to determine the most convenient experimental conditions for the silver-catalyzed exchange reaction. Above 600° with very small amounts of silver powder, the velocity of the exchange reaction was so high that it was difficult to make accurate rate measurements. In a typical experiment at 650° with 50 mg of silver powder, the oxygen-16–oxygen-18 mixture was at isotopic equilibrium in less than 10 min. Below 600°, although convenient rates were observed, the reproducibility was poor. This is probably due to partial sintering and

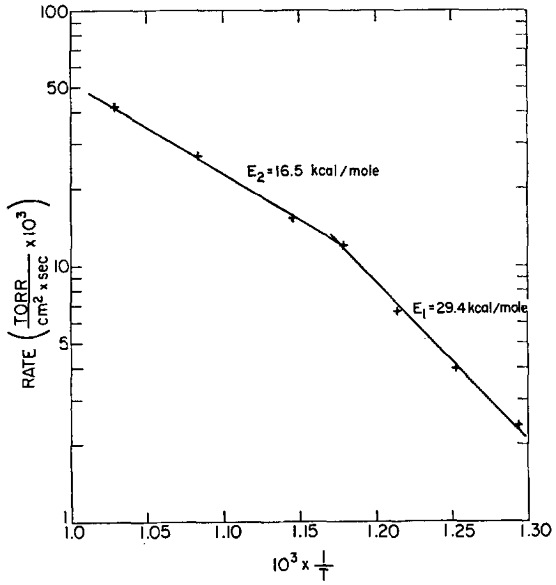

FIG. 1. Arrhenius plot for $P_{O_2} = 50$ torr.

subsequent changes in the surface area of the silver powder. These difficulties were eliminated when silver wire was used in lieu of powder and the reproducibility from experiment to experiment was excellent. Therefore, the following experiments were carried out with silver wire as the catalyst, with a surface area from 2.96 to 35.0 cm^2.

Homomolecular Exchange

The rate of the homomolecular oxygen exchange reaction was followed by measuring the decrease in the ratio ($O^{18}O^{18}/O^{18}O^{16}$) of mass $^{36}/_{34}$ as a function of time. The rate is conveniently calculated from the equation

$$R = [-2.3P_{O_2}][\log (1 - F)]/[St] \quad (1)$$

where P_{O_2} is the total pressure of oxygen in the reaction system, S is the surface area of silver catalyst and t is the time. The fraction of exchange F, at any time t can be expressed as

$$F = (N_0 - N_t)/(N_0 - N_\infty) \quad (2)$$

where N_t is the 36-to-34 mass ratio at any time t, N_0 and N_∞ are the initial and final ratios ($O^{18}O^{18}/O^{18}O^{16}$). The value of N_∞ was calculated by assuming a statistical distribution of oxygen-18 in the gas phase with an equilibrium constant of 4.00 for the reaction

$$O_2^{16} + O_2^{18} = 2O^{16}O^{18} \quad (3)$$

The method of calculation for the half-lives for the reaction, the order of the reaction with respect to oxygen pressure, and the apparent rate constant were the same as reported elsewhere (*8*). The rate of exchange was calculated by means of Eq. (1) and each rate constant reported is the average of a triplicate measurement for a minimum of 80% of the exchange reaction. The average deviation in the rate constants is less than 3% and the specific catalytic activity of the silver wire was reproducible within these limits.

The apparent activation energy for the exchange process was obtained from the variation in the rate constants as a function of temperature at constant oxygen pressure. A typical plot of the rate constant as a function of the reciprocal of the absolute temperature at 50 torr is shown in Fig. 1. Similar plots were obtained for other pressures between 15 and 100 torr. Variation in total system pressure resulted in only small changes in the activation energy. As can be seen from Fig. 1, however, two distinct ranges of activation energies are observed.* The resulting energies were 29.4 ± 1.3 kcal/mole for the range 500–575 and 16.5 ± 0.5 kcal/mole for the temperature range 575–700°C.

Since the rate of the reaction, but not the activation energy, was particularly sensitive to pressure in the range 15–100 torr, the order of the reaction with respect to pressure was determined from the change in rate as a function of pressure at constant temperature, as is shown by Eq. (4)

$$R = k[P_{O_2}]^n \tag{4}$$

where R is the observed rate as measured by the first order exchange law given in Eq. (1). The specific rate constant and the order of the reaction with respect to the exchange species as given in Eq. (4) can be determined from the intercept and slope of a graph of log R vs log P_{O_2}. Typical plots at 650° and 550° are shown in Fig. 2. Exact solution of Eq. (4) with unit weights for each datum point was obtained by means of standard least-squares techniques. The order of the reaction, n, was 0.52, 0.46, and 0.22 at 500–550°, 575°, and 600–700°, respectively. The primary change in order of the reaction occurs in the 560–590° range.

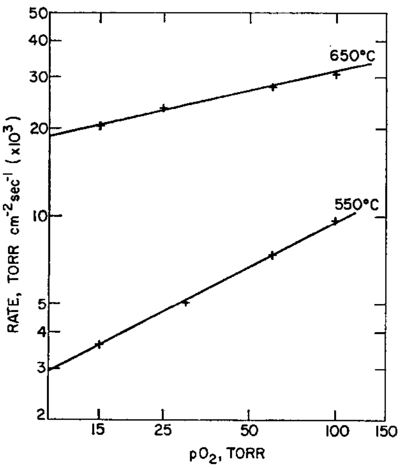

Fig. 2. Log-log plot of the exchange rate R as a function of oxygen pressure.

The homogenity of the silver surface with respect to catalysis of the homomolecular oxygen exchange reaction was determined by changing the total surface area† of the catalyst at 450° and 50 torr. With silver wire in the range of 3–20 cm² total surface area, the rate is directly proportional to the surface area.‡ No such direct proportionality was observed in the case of silver powder. These results are summarized in Table 1.

TABLE 1

The Rate of Exchange of Oxygen Isotopes as a Function of Silver Catalyst[a]

Silver wire, 8.2 cm²/gm		Silver powder, 900 cm²/gm	
Total surface area (cm²)	Rate (torr/sec)	Total surface area (cm²)	Rate (torr/sec)
2.96	1.4×10^{-3}	18.65	6.6×10^{-3}
5.01	2.4×10^{-3}	37.24	1.1×10^{-2}
11.34	5.3×10^{-3}	81.03	2.3×10^{-2}
20.52	9.8×10^{-3}	156.2	3.8×10^{-2}
28.15	1.2×10^{-2}	321.6	7.1×10^{-2}
35.00	1.5×10^{-2}	—	—

[a] Measured at 450° and 50 torr. The rates have not been normalized by the surface area of the silver metal.

Hetermolecular Exchange

It has been shown that neither Vycor nor quartz exchange oxygen with gaseous oxygen in an unpacked vessel below 950° (*8, 9, 11, 12*). According to Paladino and co-workers even at 1350° in a period of 4 hr less than 1% exchange occurs.

In the presence of silver wire, however, the exchange is measurable even at 600°. The results of two typical experiments are shown in Fig. 3 where the percent of oxygen exchange is plotted as a function of

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* The activation energies were computed by means of a nonlinear least-square computer program at the Computer Science Center of the University of Maryland.

† The same silver wire was used throughout the experiments and only the sample size was changed to increase the surface area.

‡ Removal of the silver wire from the pretreated vessel followed by an oxygen exchange experiment resulted in no enhancement. Thus, it would appear that the possibility of transfer of silver metal to the walls of the vessel or surface of the salt can be ruled out.

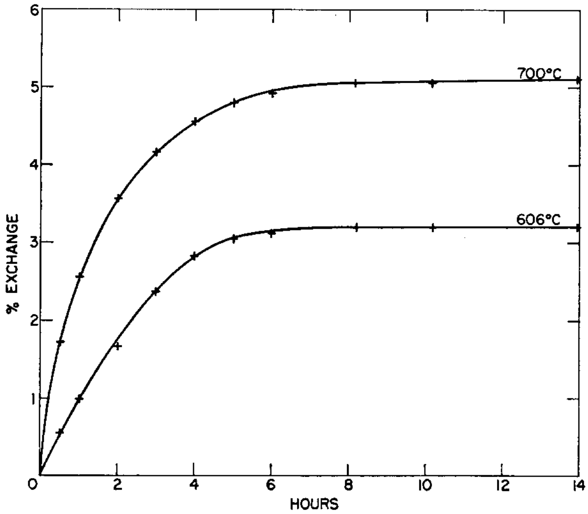

FIG. 3. Silver-catalyzed oxygen exchange with glass.

time at 606° and 700°. Initially the rate is very rapid but within several hours it levels off to a constant value. This type of curve is indicative of a fast surface reaction which becomes diffusion-controlled as the reaction proceeds.

Another series of experiments was carried out where the effect of silver wire on the rate of exchange reaction between gaseous oxygen and certain oxygen-containing salts was studied. The results with silver wire with a surface area of 5 cm² are presented in Table 2, where the half-lives of the catalytic exchange reaction between oxygen gas and Na_2CrO_4, Na_2MoO_4, or Na_2SO_4 are compared with the noncatalytic reactions (*9*). The results reported here are only those which have a direct bearing on the interpretation of the data presented earlier in this study. The results of the detailed investigation will be published elsewhere.

TABLE 2
HETEROMOLECULAR EXCHANGE REACTION BETWEEN OXYGEN GAS AND CERTAIN OXYGEN-CONTAINING SALTS

Temperature (°C)	Half-life (min)		
	Na_2MoO_4	Na_2CrO_4	Na_2SO_4
	Catalytic[a]		
460	603	468	—
500	192	226	—
540	115	132	—
606	53	76	—
	Noncatalytic		
750	—	—	670
680	—	1730	—
698	—	563	—
712	—	168	—
746	3570	—	2230
778	770	—	—
810	230	—	725

[a] With silver wire catalyst of 5-cm² surface area.

DISCUSSION

The actual isotope exchange process represents only one of the many steps in the complex catalytic exchange process and it is not necessarily the rate-determining step of the overall reaction. At least two additional steps, chemisorption and desorption, must be considered for a detailed interpretation of the isotope exchange reaction. The physical adsorption–desorption process is very rapid at low temperatures and can be neglected as a limiting step in the reactions reported here. Although surface defects and diffusion effects may influence the exchange reaction, the data in Table 1 and the linearity of each individual experiment for a minimum of 80% of the reaction seem to indicate that if these effects are present, they are only of minor importance.

Let us consider first the adsorption process and derive its possible role in the isotope exchange reaction. From the results of a variety of different measurements applied to the study of the interaction between the diatomic molecules H_2, O_2, and N_2 on various metal surfaces such as Pt, W, Au, and Ag, it is generally accepted that atomization of the molecular species occurs (*13*).

The most probable mechanism for the atomization of oxygen on metallic silver would appear to be the formation of the molecule-ion, O_2^-, by electron transfer from a silver atom. This would be followed by dissociation of this species to form charged or neutral oxygen atoms

$$O_2(g) + \text{surface electron} \rightarrow O_2^-(\text{ads}) \rightarrow O^-(\text{ads}) + O(\text{ads}) \quad (5)$$

The existence of the adsorbed species O^{2-} as proposed by Czanderna (*4*) would appear to be unlikely under our experimental conditions. This is also supported by the results of Vol and Shishakov (*14*) who have shown by electron diffraction studies that silver peroxide rather than a simple oxide is formed on the surface of silver metal which is contained in an oxygen atmosphere.

The chemisorption of oxygen also appears to be a very rapid process. Czanderna (*4*) has measured the rate of both adsorption and desorption of oxygen on silver powder and calculated the appropriate activation energies. At 100°C the activation energy necessary for complete coverage of the silver surface with a single layer of oxygen atoms was less than 3 kcal/mole. However, the formation of this atomic layer itself cannot be the rate-determining step. At temperatures above 200° with multilayer surfaces, the desorption process was found to be much slower than the adsorption process and required an activation energy of about 25 kcal/mole. It is possible, however, at higher temperatures even though the adsorbed oxygen atoms become considerably more mobile, that this mobility is still rate-determining.

In view of our results on the marked catalytic effect of silver wire on the heterogeneous exchange reaction between oxygen gas and Vycor, quartz and oxygen-containing salts, it would appear that relatively active oxygen species are desorbed from the silver surface, since in the experiments reported here the exchange reaction *cannot* occur on the silver surface. To our knowledge this would be the first experimental verification of the desorption process involving energetically active species. This could possibly account for the difficulty in earlier attempts to explain the various silver-catalyzed oxidation reactions; our results would seem to suggest that in addition to the catalytic reaction on the surface it is necessary to consider the corresponding gaseous phase reaction (*15*). This interpretation would also be useful for reactions in which the reducing agent is known to be adsorbed on silver wire.

The production of active oxygen species in the form of molecules in the first electronically excited state $^1\Delta_g$ has been reported by Haugstrom and Tate (*15*) and by Carpenter and Mair (*16*) when oxygen gas interacts with hot platinum or gold filaments. In the latter case, it is suggested that "some impurity" in the gold, catalyzed the production of the excited species since their concentration increased with increasing impurity content of the gold. The main impurity reported was silver and it would appear that the formation of active oxygen could be directly ascribed to the silver content of the gold filaments. The energy of the $^1\Delta_g$ state is 23 kcal/mole above the ground state, a value well in the range of possibility for formation under the experimental conditions reported here. Vibrationally excited ground-state oxygen molecules with relatively long half-lives which could be formed by the recombination of oxygen atoms, could also be present, as suggested by Lipcomb and Norish (*17*). Although the exact form of the active species formed when oxygen interacts with silver wire cannot be answered at this point, the existence of such a species in the gaseous phase appears to have been conclusively demonstrated by the experiments reported here.

The change in the activation energy at about 580°, as shown in Fig. 1, coincides with the change in the pressure dependence of the exchange process, which seems to suggest that the homomolecular isotopic exchange reaction proceeds by somewhat different mechanisms at different temperatures. One might consider the process in the range 525–575°C which has an activation energy of 29.4 ± 1.3 kcal/mole as a measure of the rate of desorption of oxygen where removal from the surface is governed by the bonds formed between the oxygen and the silver. The order of the reaction was found to be 0.52 in this temperature range, which indicates that the desorption process would be proportional to the concentration of oxygen atoms on the surface, since this concentration itself is a function of the square root of the oxygen pressure. As the temperature increases, the mobility of the adsorbed layer also increases and the metal–oxygen bond is relatively weaker, thus the rate of the desorption process should be considerably increased. The experimental observation is that a process with a lower activation (16.5 ± 0.5 kcal/mole) and a reaction order of only 0.20 occurs, which would suggest that this process is governed neither by the mobility of the oxygen atoms on the surface or by the rate of exchange itself.

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