Reports of the Academy of Sciences of the USSR

Corresponding Member of the Academy of Sciences of the USSR G. K. BORESKOV, A. V. KHASIN,

1965

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR

1965. Volume 164, No. 3

PHYSICAL CHEMISTRY

Corresponding Member of the Academy of Sciences of the USSR G. K. BORESKOV, A. V. KHASIN,
T. S. STAROSTINA

ISOTOPIC EXCHANGE OF OXYGEN ON SILVER FILMS

Silver serves as a catalyst in a number of important processes of selective oxidation of organic substances, such as the oxidation of ethylene to ethylene oxide, of methanol to formaldehyde, etc. In resolving the question of the mechanism of oxidative catalysis on silver, it is necessary to know the state of adsorbed oxygen. The state of oxygen on silver has been studied by various methods by many investigators ([1]-[10]), but there are considerable discrepancies on a number of fundamental questions, in particular concerning the forms of adsorbed oxygen.

In order to investigate the character of the bond of oxygen on the surface of silver, we studied the kinetics of reactions of isotopic exchange of adsorbed oxygen with gaseous oxygen and of homomolecular isotopic exchange of oxygen. The kinetics of exchange were investigated in a static vacuum apparatus. Isotopic analysis of oxygen was carried out on an MI-1305 mass spectrometer. The admission of oxygen into the ion source of the mass spectrometer took place directly from the reaction volume through a glass capillary and could be carried out either continuously or periodically. The films were prepared in the reaction vessel by evaporation from a silver wire spiral (99.99% Ag; wire diameter 0.3 or 0.5 mm), heated by an electric current, in a vacuum of 10^{-7}–10^{-6} mm Hg.

Condensation of silver was carried out at −195° or 20°. Immediately after deposition, the films were heated in vacuum: films condensed at 20° were heated for 3 hours at 250 or 300°; a film condensed at −195° was first warmed to room temperature and then heated for 3 hours at 200°.

According to measurements of low-temperature krypton adsorption ([11]), the surface of films deposited at 20° was 120–160 cm^2. A film condensed at −195° initially had a surface area of 360 cm^2, but subsequently it was heated in oxygen at 250°, as a result of which its surface decreased to 300 cm^2 and, upon subsequent heating under the same conditions, to 250 cm^2.

Fig. 1

Figure 1: Fig. 1

Adsorption of oxygen enriched with the isotope O^{18} (43% O^{18}) was carried out on freshly prepared films at the following temperatures: 200° in the experiment with the film condensed at −195°, and 250° in experiments with films condensed at 20°.

Half an hour after the start of the experiment, adsorption was essentially complete, and subsequently only very slow uptake occurred. During this time, at the indicated temperatures, the film condensed at −195° adsorbed 0.7 monolayer, and the films condensed at 20°, 2-3 monolayers. In calculating the monolayer value it was assumed that, for complete coverage of 1 cm^2 of silver surface, $1.2 \cdot 10^{15}$ oxygen atoms are required.

After the adsorption measurement, the films were kept for 12-40 hours at the indicated adsorption temperatures and at pressures of 0.04-0.15 mm Hg in

enriched oxygen. In this case, a significant decrease in the concentration of O^{18} in the gaseous oxygen was observed. This indicated that, even before adsorption, the films contained oxygen of natural isotopic composition. According to the estimate made (from the decrease in the O^{18} content in the gas phase), its amount reached several monolayers. In all probability, this oxygen, despite preliminary degassing, remained in the silver spiral and was absorbed in the process of silver condensation.

Fig. 1. Increase in the concentration of O^{18} in the gas phase at 200°. 1—after holding at 200° (pressure $P = 0.12$ mm Hg, $N = 2.4 \cdot 10^{-6}$ mol, surface $S = 360$ cm^2, $C_0' = 36.9\%$); 2—after holding at 250° ($P = 0.12$ mm, $N = 2.4 \cdot 10^{-6}$ mol, $S = 300$ cm^2, $C_0' = 41.0\%$).

During the holding of the films in oxygen, enrichment of the oxygen of the films with the heavy isotope took place.

On the enriched films, isotopic exchange was carried out with gaseous oxygen of natural composition. For this purpose the enriched oxygen was pumped out of the reaction volume at room temperature, and oxygen of natural isotopic composition was admitted into it. Then the reaction vessel was placed in a furnace preheated to the temperature of the experiment, and the reaction of isotopic exchange of the adsorbed oxygen with the gaseous oxygen proceeded. During the experiment, isotopic analysis of the oxygen was carried out, and during the first hour it was usually practically continuous. As a result of the measurements we obtained curves for the increase in the concentrations of $O^{18}O^{18}$ and $O^{16}O^{18}$ in the gaseous oxygen.

To determine the content of O^{18} in the adsorbed oxygen at the initial moment of the reaction, we used the results of measurements of the exchange rate during the preliminary holding of the films in enriched oxygen. The rate of isotopic exchange at the end of the treatment of the film with heavy oxygen is $N(dC/d\tau)_{\tau_k} = v(C'_0 - C_k)$, and at the beginning of the exchange with natural oxygen

$$N(dC/d\tau)_{\tau_0} = v(C'_0 - C_0), \tag{1}$$

where N is the amount of gaseous oxygen in the system; τ is time; C is the fraction of O^{18} in the gaseous oxygen; C_0 is the fraction of O^{18} in the gaseous oxygen, and C'_0 is the fraction of O^{18} in the adsorbed oxygen at the initial moment of isotopic exchange with natural oxygen; C_k is the fraction of O^{18} in the gaseous oxygen at the end of the preceding treatment; v is the exchange rate. Solving these two equations, we find C'_0 and v. Earlier, when calculating from the data of the first experiments the exchange rates and the amount of oxygen that had exchanged, we took C'_0 to be equal to the content of O^{18} in the initial enriched oxygen, which considerably exceeded the actual value; as a result, understated values of the indicated quantities were obtained ([9]). The kinetics of the isotopic-exchange reaction was studied at $200, 250°$ and pressures of 0.1-0.6 mm Hg. In Fig. 1A (curve 1) the increase in the concentration of O^{18} is shown at

200° in the experiment with a film condensed at −195°, after adsorption and holding in oxygen at 200°. After completion of the reaction, the film was held in enriched oxygen at 250°, and the kinetics of isotopic exchange were again measured at 200° (Fig. 1, curve 2).

The cause of the decrease in the activity of the film after treatment with oxygen at 250° is possibly an increase in the oxygen content in the near-surface layers of the film.

As can be seen from Fig. 1b, the kinetics of isotopic exchange at 200° satisfy a first-order equation

$$\frac{N \cdot N'}{N + N'} \ln \frac{C_\infty - C_0}{C_\infty - C} = v\tau, \tag{2}$$

where N' is the amount of silver oxygen participating in the exchange; C_∞ is the fraction of O^{18} in gaseous oxygen corresponding to the isotopic equilibrium of the system; the remaining letter designations have the same meaning as in (1). Equation (2) is obtained by integrating equation (1). From the balance equation $NC_0 + N'C'_0 = (N + N')C_\infty$ we find that the amount of oxygen in the film participating in the exchange, N', in the first experiment is 2.8 and in the second 2.0 monolayers. Thus, the indicated amount of silver oxygen under these conditions proves to be equivalent with respect to exchange with gaseous oxygen, and this indicates its energetic uniformity.

The ratios of the initial rates of increase of the isotopic molecules $O^{16}O^{18}$ and $O^{18}O^{18}$ in the experiments under consideration (Fig. 2) are 3.5 and 3.2, and

Figure 2 and Figure 3

Figure 2: Figure 2 and Figure 3

are close to the values that would be observed upon desorption of equilibrium oxygen: at initial O^{18} concentrations equal to 36.9 and 41.0%, the equilibrium ratios are 3.4 and 2.9.

As the degree of exchange increases, this ratio increases, but continues to correspond to desorption of an equilibrium gas.

This result indicates an adsorption–desorption mechanism of exchange with a very high rate of redistribution of isotopic atoms in the adsorbed oxygen.

Fig. 2. Increase in the concentrations of $O^{16}O^{18}$ and $O^{18}O^{18}$ at the beginning of experiments at 200° (the same experiments as in Fig. 1)

Fig. 3. Increase in the concentration of O^{18} in the gas phase at 250°: 1 —in the experiment with a film condensed at −195° ($P = 0.12$ mm Hg, $N = 2.3 \cdot 10^{-6}$ mol, $S = 250$ cm^2, $C'_0 = 42.6\%$); 2 —in the experiment with a film condensed at 20° ($P = 0.11$ mm Hg, $N = 2.3 \cdot 10^{-6}$ mol, $S = 120$ cm^2, $C'_0 = 33.6\%$)

At 250° (Fig. 3), about 1-2 additional monolayers of oxygen enter into exchange with gaseous oxygen, so that the total amount participating in the exchange is not less than 3-4 monolayers. At this temperature the reaction kinetics are not described by equation (2), since the O additionally entering into exchange exchanges at a lower rate.

The specific exchange rates are given in Table 1; from its data it follows that the film condensed at −195°, with the same preliminary treatment with oxygen, does not differ from the other films with respect to exchange. The apparent activation energy of the reaction is 31 ± 2 kcal/mol. The order of the exchange with respect to oxygen pressure at 250° is 0.3.

Homomolecular oxygen exchange was studied on films after experiments on isotope exchange had been carried out. The films were preliminarily held at the reaction temperature in oxygen with the same content of O^{18} as in the reaction mixture (a mixture of equal volumes of enriched and natural oxygen), until isotopic equilibrium was reached. The experiments were carried out at 225, 250, 300° and pressures of 0.1-0.7 mm Hg. The exchange rates were calculated from the first-order equation (12).

Table 1

Temperature of condensation of Ag vapors during film preparation, °C	Temperature of preliminary holding of film in O_2, °C	Reaction of isotope exchange of adsorbed oxygen with gaseous oxygen: reaction temperature, °C	Reaction of isotope exchange of adsorbed oxygen with gaseous oxygen: pressure, mm Hg	Reaction of isotope exchange of adsorbed oxygen with gaseous oxygen: specific exchange rate, mol/sec × cm^2	Reaction of isotope exchange of adsorbed oxygen with gaseous oxygen: apparent activation energy of reaction, kcal/mol	Reaction of homomolecular isotope exchange: reaction temperature, °C	Reaction of homomolecular isotope exchange: pressure, mm Hg	Reaction of homomolecular isotope exchange: specific exchange rate, mol/sec · cm	Reaction of homomolecular isotope exchange: apparent activation energy, kcal/mol
−195	200	200	0.12	$4.4 \cdot 10^{-14}$	–	–	–	–	–
−195	250	200	0.12	$1.8 \cdot 10^{-14}$	31	225	0.11	$0.94 \cdot 10^{-13}$	34
−195	250	250	0.12	$4.4 \cdot 10^{-13}$	–	250	0.11	$4.9 \cdot 10^{-13}$	–
20	250	200	0.11	$1.5 \cdot 10^{-14}$	31	250	0.10	$(3.1–3.7) \cdot 10^{-13}$	29–32
20	250	250	0.11	$3.7 \cdot 10^{-13}$	–	300	0.10	$(4.1–4.7) \cdot 10^{-12}$	–

As is seen from the data of Table 1, the initial exchange rates for the isotope-exchange reaction coincide with the exchange rates for the homomolecular-exchange reaction; the activation energies for both reactions also coincide. The order of homomolecular exchange at 250°, as in the case of the isotope-exchange reaction, is 0.3.

Thus, it may be concluded that both reactions proceed by one and the same mechanism—an adsorption-desorption mechanism. This result confirms the equality of the rates of desorption and exchange observed by Sandler and Hickam (10).

The small value of the order indicates a significant (>0.5) degree of coverage under the conditions of our experiments. Nevertheless, at 200° more silver oxygen enters into exchange than can be present on the surface, and the fact that this oxygen is equivalent in exchange with the gas phase indicates its high mobility.

Institute of Catalysis
Siberian Branch of the Academy of Sciences of the USSR

Received
27 I 1965

REFERENCES

1. M. I. Temkin, N. V. Kulkova, DAN, **105**, No. 5, 1021 (1955).
2. I. N. Pospeleva, A. A. Rakov, S. Ya. Pshezhetskii, ZhFKh, **30**, No. 7, 1433 (1956).
3. R. G. Meisenheimer, A. W. Ritchie et al., Solid-Gas Interface, Proc. of the II Intern. Congress of Surface Activity, **2**, 1957.
4. L. Ya. Margolis, Izv. AN SSSR, OKhN, 1959, No. 2, 225.
5. N. V. Kulkova, M. I. Temkin, ZhFKh, **36**, No. 8, 1731 (1962).
6. V. E. Ostrovskii, I. R. Karpovich et al., ZhFKh, **37**, No. 11, 2596 (1963).
7. J. Bagg, L. Bruce, J. Catal., **2**, No. 2, 93 (1963).
8. Ya. M. Fogel, B. T. Nadykto et al., ZhFKh, **38**, No. 10, 2397 (1964).
9. G. K. Boreskov, A. V. Khasin, Kinetika i kataliz, **5**, No. 5, 956 (1964).
10. Y. L. Sandler, W. M. Hickam, Dokl. at the III International Congress on Catalysis, Amsterdam, 1964.
11. R. H. Beebe, J. B. Beckwith, J. M. Honig, J. Am. Chem. Soc., **67**, No. 9, 1554 (1945).
12. M. A. Avdeenko, G. K. Boreskov, M. G. Slinko, Problems of Kinetics and Catalysis, **9**, 61 (1957).

Note: Figure translations are in progress. See original paper for figures.