Mechanism of the Exchange Reaction of Oxygen Atoms between Gaseous Oxygen and Water Vapor Catalyzed by Calcium Oxide

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(Received April 23, 1956)

Introduction

In previous papers[1] where we studied the rate R of the exchange reaction of oxygen atoms between gaseous oxygen and water vapor from measurements of the rate of the isotopic exchange reaction of oxygen isotopes catalyzed by chromic oxide, we concluded that the rate R remains constant irrespective of the feed rate of the reacting gaseous mixture so long as it maintained a rate higher than about 30 cc./sec.·cm^2. In that case the rate of the exchange reaction should be controlled by some one or more of the surface processes, i. e. adsorption of reactants, chemical reaction on surface, and desorption of products. Then by observing the change in rate of the exchange reaction under various mixing molar ratios of the reacting gases $\alpha=O_2/H_2O$ and under the assumption that only one chemical step is rate controlling, we can examine the mechanism of the reaction by the method developed by Langmuir-Hinshelwood and later extended by Hougen[2]. The result obtained with chromic oxide catalyst was read at the 4th Symposium of Catalysis of the Chemical Society of Japan held in Sapporo on July 24, 1955[3]. Now, this method has been applied to the reaction catalyzed by calcium oxide and the results compared with that obtained with chromic oxide.

Experimental and Analytical Procedure

The experimental procedure was the same as described in the previous paper[1]. A quartz tube of 1.6 cm. inside diameter was used in a vertical position. The rate R, number of exchange per sec. per cc. of the reactor, was calculated by the following relation:

$$R=\frac{6.155\cdot10^{19}}{Z}\frac{\alpha}{(2\alpha+1)(\alpha+1)}F\{-\log(1-x)\} \quad (1)$$

Here x is the conversion, net fraction of the isotopic exchange reaction to equilibrium, F is the feed rate of the gaseous mixture in cc. (S.C.)/sec., and Z is the height of the catalyst bed in cm.

The calcium oxide catalyst was prepared from commercial calcium oxide of chemically pure grade. The blocks of calcium oxide were crushed to particles of 2–3 mm., and calcined at 850°C for four hours under oxygen gas flow.

As the foundation for analysis of experimental results, we assume, as has been done by many authors[4], that all adsorption sites on the catalyst

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[*] The main part of this paper was presented at the 9th Annual Meeting of the Chemical Society of Japan on April 2, 1956, Kyoto.

[1] S. Sakata and N. Morita, This Bulletin, **29**, 230 (1956); *Chem. Eng.* (*Japan*), **19**, 64 (1955).

[2] O.A. Hougen and K.M. Watson, *Ind. Eng. Chem.*, **35**, 529 (1943); "Chemical Process Principles", John Wiley & Sons, Inc., New York, N.Y. (1950).

[3] S. Sakata and N. Morita, *Shokubai* Catalyst, **12**, 80 (1955).

[4] O.A. Hougen and K.M. Watson, l.c.; H.F. Rase and R.S. Kirk, *Chem. Eng. Progr.*, **50**, 35 (1954).

surface behave similarly and that the interfacial activities of components of the reacting gaseous mixture are equal to their partial pressures in the bulk phase Then, (I) if we consider the case in which molecular adsorption of both reactants occur, the equilibrium concentrations of molecularly adsorbed oxygen and water on the surface, c_{O_2} and c_{H_2O}, and equilibrium concentration of vacant site on the surface, c_l, all in number of sites per unit mass of catalyst, can be expressed by

$$c_{O_2}=p_oK_oL/(1+p_oK_o+p_wK_w) \qquad (2)$$

$$c_{H_2O}=p_wK_wL/(1+p_oK_o+p_wK_w) \qquad (3)$$

$$c_l=L/(1+p_oK_o+p_wK_w) \qquad (4)$$

where p_o is the partial pressure of oxygen in atm. and p_w the same of water, K_o is the adsorption equilibrium constant of oxygen in atm.$^{-1}$ and K_w the same of water, and L is the total number of active sites on the surface per unit mass of catalyst. During the exchange reaction the chemical concentration of reactants, i.e. p_o and p_w, do not change and therefore the values of c's remain constant. Consequently, (A) when the rate of molecular adsorption of oxygen controls the rate of the exchange reaction, it can be expressed by $R=kp_oc_l=kp_oL/(1+p_oK_o+p_wK_w)$, or $p_o/R=(1/kL)+(K_o/kL)p_o+(K_w/kL)p_w$, where k is the adsorption velocity constant for oxygen. Taking total pressure p_o+p_w as a unit pressure which is kept constant during a series of experiments, we can write $p_o=\alpha/(\alpha+1)$ and $p_w=1(\alpha+1)$. Then we obtain

$$\alpha/R=(a+b)\alpha+(a+c) \qquad (5)$$

where a, b and c are positive constants and $a=1/kL$, $b=K_o/kL$ and $c=K_w/kL$. On the contrary, (B) when the rate of desorption of molecularly adsorbed oxygen is controlling, we obtain $R=kc_{O_2}=kp_oK_oL/(1+p_oK_o+p_wK_w)$, where, in this case, k is the desorption velocity constant for oxygen. Then we can write

$$\alpha/R=(a+b)\alpha+(a+c) \qquad (6)$$

where a, b and c are positive constants different from those in Eq. (5) and $a=1/kK_oL$, $b=1/kL$ and $c=K_w/kK_oL$.

By the same reasoning we can obtain the following expression, (C, D) when adsorption or desorption of water is rate-controlling

$$1/R=(a+b)\alpha+(a+c) \qquad (7)$$

Finally, (E) when the surface chemical reaction is controlling, R is proportional to the surface concentration of pairs of adsorbed oxygen and water molecules in adjacent positions. This concentration is equal to $sc_{O_2}c_{H_2O}/L$, where s is the number of equidistant active sites adjacent to each site. Therefore, $R=ksp_op_wK_oK_wL/(1+p_oK_o+p_wK_w)^2$, and by rearrangement we obtain

$$\sqrt{\alpha/R}=(a+b)\alpha+(a+c) \qquad (8)$$

where. $a=1/\sqrt{ksK_oK_wL}$, $b=K_o/\sqrt{ksK_oK_wL}$ and $c=\sqrt{K_w/ksK_oL}$.

(II) When oxygen is adsorbed with dissociation, its equilibrium concentration c_O and that of water and of vacant sites c_{H_2O} and c_l are expressed by

$$c_O=L\sqrt{p_oK_o}/(1+\sqrt{p_oK_o}+p_wK_w) \qquad (9)$$

$$c_{H_2O}=p_wK_wL/(1+\sqrt{p_oK_o}+p_wK_w) \qquad (10)$$

$$c_l=L/(1+\sqrt{p_oK_o}+p_wK_w) \qquad (11)$$

In order that oxygen molecules can be atomically adsorbed, dual adsorption sites are necessary and their concentration can be expressed by $c_{l_2}=sc_l^2/2L$. Therefore, (A) when the rate of adsorption of oxygen with dissociation controls the rate of the exchange reaction, we have the relation $R=kp_oc_{l_2}=(ksp_oL/2)/(1+\sqrt{p_oK_o}+p_wK_w)^2$, and then

$$\sqrt{\alpha(\alpha+1)/R}=a\alpha+b\sqrt{\alpha(\alpha+1)}+(a+c) \qquad (12)$$

For the case (B) where the rate of recombination of atomically adsorbed oxygen to molecule is controlling we obtain the same expression as Eq. (12).

In the same way we can obtain the expressions (C, D) when adsorption or desorption of water is controlling

$$1/R=a\alpha+b\sqrt{\alpha(\alpha+1)}+(a+c) \qquad (13)$$

and (E) when chemical reaction on the surface is controlling

$$\sqrt{\sqrt{\alpha(\alpha+1)}/R}=a\alpha+c\sqrt{\alpha(\alpha+1)}+(a+c) \qquad (14)$$

(III) We have to consider adsorption of water vapor with dissociation. In this case the state of adsorption is HOl+Hl, where l indicates adsorption site. However, adsorption of hydrogen atom may occur at the oxygen atom on the surface of metallic oxide, and, therefore, as an additional assumption, we consider the state of adsorption to be HOl+HOl, both behaving similarly. Then we have the forms which are summarized in Table I for the relation between the rate of exchange reaction and the mixing ratio of reactants according as (A, B) adsorption or desorption of oxygen or (C, D) adsorption of water with dissociation or recombination or (E) chemical reaction on surfaces is rate-controlling.

(IV) We have also the cases where both oxygen and water are absorbed with dissociation and (A, B) adsorption of oxygen with dissociation or recombination or (C, D) adsorption of water with dissociation or recombination or (E) some one of the surface chemical reactions is rate-controlling.

The equations from these postulated mechanisms are summarized in Table I. By comparing these forms with experimental results we can select one or more of them as the probable mechanism. We can consider mechanisms other than those listed in Table I such as when one reactant in the gaseous phase reacts with another adsorbed reactant. However, we have excluded these mechanisms because for an exchange reaction to take place, there is a necessary step of dissociation which needs much more activation energy than the collision of molecules on the catalyst surface. It is a fact that most of the observed rates of exchange reaction are less than one-millionth of the collision number of the gaseous reactant on the other surface of the catalyst.

TABLE I

SUMMARY OF EQUATIONS FROM POSTULATED MECHANISMS

Mechanism		Equation	Values of Constants		
			a	b	c
I	A	$\alpha/R=(a+b)\alpha+(a+c)$	$1/kL$	K_o/kL	K_w/kL
	B	$\alpha/R=(a+b)\alpha+(a+c)$	$1/kLK_o$	$1/kL$	K_w/kLK_o
	C	$1/R=(a+b)\alpha+(a+c)$	$1/kL$	K_o/kL	K_w/kL
	D	$1/R=(a+b)\alpha+(a+c)$	$1/kLK_w$	K_o/kLK_w	$1/kL$
	E	$\sqrt{\alpha/R}=(a+b)\alpha+(a+c)$	$1/\sqrt{ksLK_oK_w}$	$K_o/\sqrt{ksLK_oK_w}$	$\sqrt{K_w/ksLK_o}$
II	A	$\sqrt{\alpha(\alpha+1)/R}=a\alpha+b\sqrt{\alpha(\alpha+1)}+(a+c)$	$\sqrt{2/ksL}$	$\sqrt{2K_o/ksL}$	$K_w\sqrt{2/ksL}$
	B	$\sqrt{\alpha(\alpha+1)/R}=a\alpha+b\sqrt{\alpha(\alpha+1)}+(a+c)$	$\sqrt{2/ksLK_o}$	$\sqrt{2/ksL}$	$K_w\sqrt{2/ksLK_o}$
	C	$1/R=a\alpha+b\sqrt{\alpha(\alpha+1)}+(a+c)$	$1/kL$	$\sqrt{K_o}/kL$	K_w/kL
	D	$1/R=a\alpha+b\sqrt{\alpha(\alpha+1)}+(a+c)$	$1/kLK_w$	$\sqrt{K_o}/kLK_w$	$1/kL$
	E	$\sqrt{\sqrt{\alpha(\alpha+1)}/R}=a\alpha+b\sqrt{\alpha(\alpha+1)}+(a+c)$	$\sqrt{1/ksL\sqrt{K_oK_w}}$	$\sqrt{\sqrt{K_o}/ksLK_w}$	$\sqrt{K_w/ksL\sqrt{K_o}}$
III	A	$\alpha/R=(a+b)\alpha+c\sqrt{\alpha+1}+a$	$1/kL$	K_o/kL	$\sqrt{K_w}/kL$
	B	$\alpha/R=(a+b)\alpha+c\sqrt{\alpha+1}+a$	$1/kLK_o$	$1/kL$	$\sqrt{K_w}/kLK_o$
	C	$\sqrt{1/R}=a\sqrt{\alpha+1}+b\alpha/\sqrt{\alpha+1}+c$	$\sqrt{2/ksL}$	$K_o\sqrt{2/ksL}$	$\sqrt{2K_w/ksL}$
	D	$\sqrt{1/R}=a\sqrt{\alpha+1}+b\alpha/\sqrt{\alpha+1}+c$	$\sqrt{2/ksLK_w}$	$K_o\sqrt{2/ksLK_w}$	$\sqrt{2/ksL}$
	E	$\sqrt{\alpha\sqrt{\alpha+1}/R}=(a+b)\alpha+c\sqrt{\alpha+1}+a$	$\sqrt{1/ksLK_o\sqrt{K_w}}$	$\sqrt{K_o/ksL\sqrt{K_w}}$	$\sqrt{\sqrt{K_w}/ksLK_o}$
IV	A	$\sqrt{\alpha/R}=a\sqrt{\alpha+1}+b\sqrt{\alpha}+c$	$\sqrt{2/ksL}$	$\sqrt{2K_o/ksL}$	$\sqrt{2K_w/ksL}$
	B	$\sqrt{\alpha/R}=a\sqrt{\alpha+1}+b\sqrt{\alpha}+c$	$\sqrt{2/ksLK_o}$	$\sqrt{2/ksL}$	$\sqrt{2K_w/ksLK_o}$
	C	$\sqrt{1/R}=a\sqrt{\alpha+1}+b\sqrt{\alpha}+c$	$\sqrt{2/ksL}$	$\sqrt{2K_o/ksL}$	$\sqrt{2K_w/ksL}$
	D	$\sqrt{1/R}=a\sqrt{\alpha+1}+b\sqrt{\alpha}+c$	$\sqrt{2/ksLK_w}$	$\sqrt{2K_o/ksLK_w}$	$\sqrt{2/ksL}$
	E	$\sqrt{\sqrt{\alpha}/R}=a\sqrt{\alpha+1}+b\sqrt{\alpha}+c$	$\sqrt{1/ksL\sqrt{K_oK_w}}$	$\sqrt{\sqrt{K_o}/ksL\sqrt{K_w}}$	$\sqrt{\sqrt{K_w}/ksL\sqrt{K_o}}$

Experimental Results and Discussion

The results obtained are tabulated in Table II. For comparison, the results obtained with chromic oxide catalyst are also included in the table. In both cases, for the lower values of α, the rate R increases with the increase in α, and for the higher values of α the rate remains almost constant irrespective of the values of α. The main differences are the lower activity and the more gradual approach to a constant value of R of calcium oxide as compared with chromic oxide. Those facts indicate that we can examine the mechanism of the exchange reaction catalyzed by calcium oxide by the same course as that of chromic oxide except for the point that the relative importance of adsorption equilibrium constants K_o and K_w may be different for both catalysts.

For selection of the probable mechanism, Hougen recommended that the constants of the equations for the various proposed mechanisms be determined, i.e. a, b and c, which must be positive, by use of the method of least squares. However, as for every one of the equations from the postulated mechanisms of groups II and IV there were two nearly parallel terms, so the probable errors of the constants which were determined by

TABLE II

Calcium Oxide

Temperature = 743°C
F = 28.9 cc./sec.·cm²
Average Total
Pressure = 769 mmHg

Exp. No.	α	$R\times10^{-18}$ atoms/ sec.·cc.
1418	0.553	4.74
1411	0.571	5.01
1414	1.142	6.21
1420	1.951	6.52
1410	2.010	6.84
1419	3.63	7.60
1412	4.60	9.37
1413	5.56	8.75
1417	7.67	8.80
1415	10.40	8.82

Temperature = 700°C
F = 29.9 cc./sec.·cm²

Exp. No.	α	$R\times10^{-18}$ atoms/ sec.·cc.
1502	0.536	2.35
1505	1.079	3.02
1501	2.040	3.56
1509	2.153	3.24
1507	3.78	3.96
1503	4.70	4.02
1504	6.43	4.41
1508	8.29	4.44
1506	10.52	4.38

Chromic Oxide

Temperature = 521°C
F = 30.1 cc./sec.·cm²
Average Total
Pressure = 783 mmHg

Exp. No.	α	$R\times10^{-18}$ atoms/ sec.·cc.
1304	0.050	2.38
1303	0.080	2.75
1302	0.082	2.64
1211	0.336	2.86
1204	0.410	4.09
1307	0.495	3.38
1107	0.842	4.44
1105	0.926	4.75
1104	0.966	4.75
1210	1.231	3.91
1202	1.337	4.11
1109	2.094	4.63
1102	2.222	4.81
1106	2.876	4.99
1201	3.30	5.43
1108	3.86	4.56
1103	4.14	4.67
1203	8.78	5.20
1301	13.12	5.01

the method of least squares were considerable. Therefore, we examined the mechanisms graphically.

First, the mechanisms in which adsorption or desorption of water is rate controlling, i.e. all of C's and D's can be excluded. In these mechanisms $1/R$ must be increased with the increase in α which is inconsistent with the experimental results.

The mechanisms of group I can be examined by plotting values of left-hand terms of the equations against α. In Fig. 1, curves I–E are the relations of $\sqrt{\alpha/R}$ vs. α. They do not indicate linear relation and the mechanism I–E can not be applied. The relation α/R vs. α is practically linear as shown by lines I–A, B in Fig. 1, and the mechanisms I–A and I–B must be reserved as probable mechanisms. We will consider these mechanisms again later.

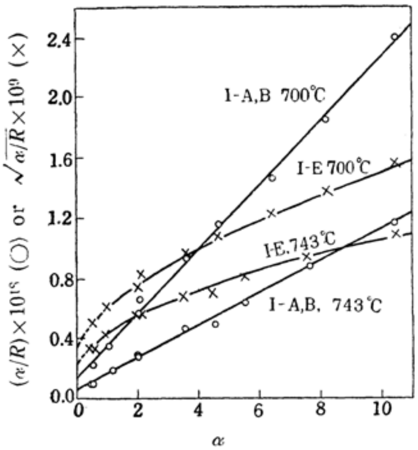

Fig. 1. Mechanisms I–A, B and I–E.

The right-hand side of each equation for the mechanisms of groups II, III and IV has two variable terms. We scrutinize these mechanisms by plotting two variables separately against the values of the left-hand terms and testing the possibility of constructing a linear combination with positive coefficients from these two curves to gain linear relation. Fig. 2 to Fig. 7 are such plottings. In examining these plottings we notice the further facts that the value of the left-hand side of each equation extrapolated to $\alpha=0$ gives $a+c$ and that the inclination of the curves for mechanisms of groups II and IV converge to $a+b$ for high values of α.

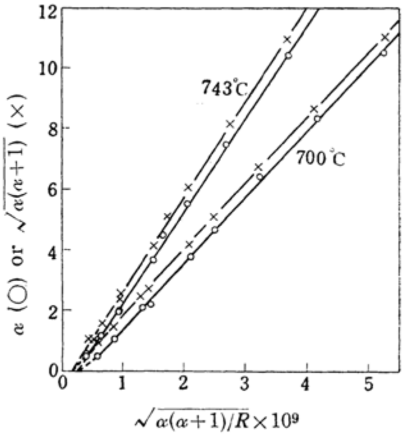

Fig. 2. Mechanisms II–A, B.

By such criterions we can easily exclude the mechanisms of II–E, III–A, B and III–E. In Fig 3 which represents the relation for mechanism II–E, both of the curves for α and $\sqrt{\alpha(\alpha+1)}$ vs. $\sqrt{\sqrt{\alpha(\alpha+1)}/R}$ are concave and can not gain combination to give linearity. In Fig. 4 for mechanisms III–A, B the relation of α vs. α/R is almost linear but $\sqrt{\alpha+1}$ vs. α/R is convex and their combination can be linear only when the values of

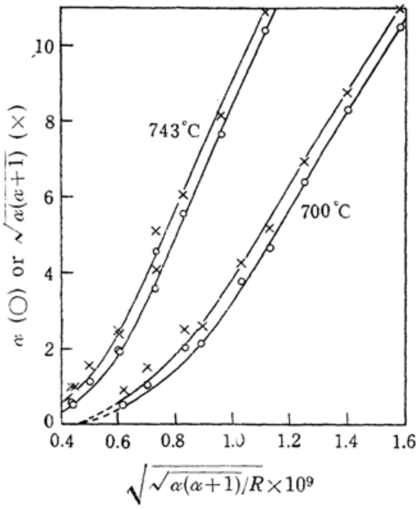

Fig. 3. Mechanism II–E.

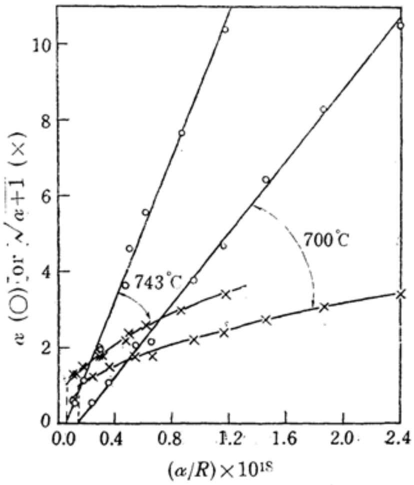

Fig. 4. Mechanisms III–A, B.

c are very small, and then this is the same as the mechanisms I-A, B. For mechanism III-E only $\sqrt{\alpha+1}$ vs. $\sqrt{\alpha\sqrt{\alpha+1}/R}$ is linear as shown in Fig. 5. To select this mechanism, a and b must be very small and then both of the extrapolated values of abscissa at $\alpha=0$ and the inclination of the straight line must be nearly equal to c. This is not the case. The abscissa values at $\alpha=0$ are less than 0.3×10^{-9} compared with the inclinations of the lines which are about 1×10^{-9}.

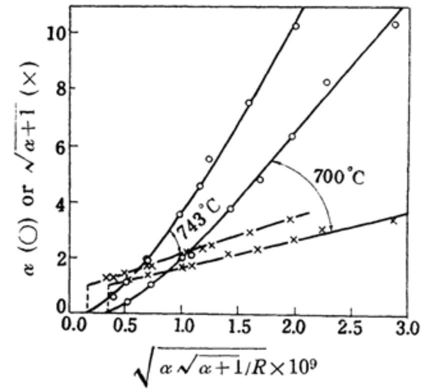

Fig. 5. Mechanism III-E.

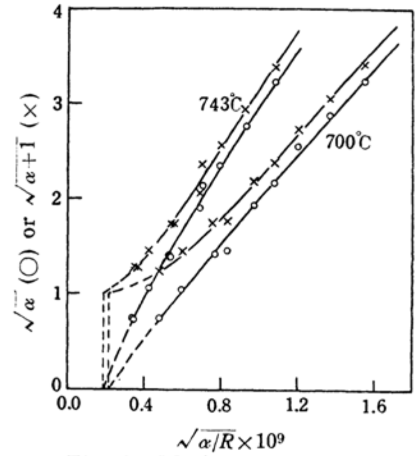

Fig. 6. Mechanisms IV-A, B.

For all other mechanisms we can not state exactly from Figs. 2, 6 and 7 their applicability or non-applicability. Therefore, we first evaluated the constants a, b and c for each mechanism by applying the two criterions noted above for the determination of $a+b$ and $a+c$ and using a pair of values on the pair of smoothed curves. And then we examined the propriety of these constants to the mechanism. Evaluated values are tabulated in Table III. For comparison, values of constants for the exchange reaction with chromic oxide catalyst are also included. Values of K_o were calculated from a and b, and K_w's from a and c. The apparent activation energies E for calcium oxide catalyst were calculated from pairs of values of a obtained at two temperatures, assuming constants values for L and s.

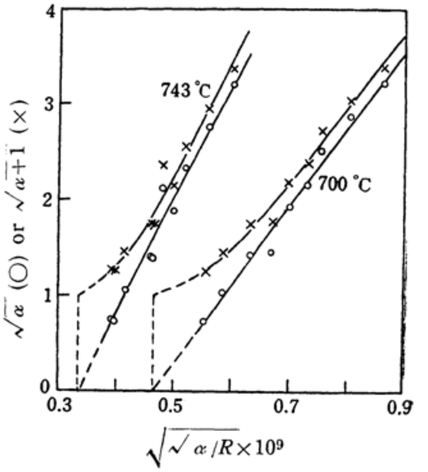

Fig. 7. Mechanism IV-E.

TABLE III

EVALUATED VALUES OF CONSTANTS

Mechanism	Catalyst	Temp. °C	$a+b$ $\times10^9$	$a+c$ $\times10^9$	a $\times10^9$	b $\times10^9$	c $\times10^9$	K_o	K_w	E kcal.
II A, B	Calcium Oxide	743	0.321	0.156	0.061	0.260	0.095	18.2	1.56	33
	〃	700	0.460	0.250	0.088	0.372	0.162	17.9	3.40	
	Chromic Oxide	521	0.439	0.112	0.094	0.345	0.018	13.5	0.19	
IV A, B	Calcium Oxide	743	0.317	0.194	0.165	0.152	0.029	0.8_5	0.03_1	7.4
	〃	700	0.458	0.213	0.179	0.279	0.034	2.4_3	0.03_6	
	Chromic Oxide	521	0.437	0.071	0.050	0.378	0.021	60.0	0.16	
IV E	Calcium Oxide	743	0.092	0.335	0.038	0.054	0.397	2.0_2	109	22
	〃	700	0.134	0.465	0.050	0.084	0.415	2.8_1	69	
	Chromic Oxide	521	0.117	0.270	negative	—	—	—	—	
			$\times10^{18}$	$\times10^{18}$						
I A, B	Calcium Oxide	743	0.105	0.065						
	〃	700	0.212	0.145						
	Chromic Oxide	521	0.204	0.040						

Taken from the criterion that a, b and c must be positive, all the mechanisms in Table III, except IV–E for chromic oxide, are applicable. However, mechanism IV–E for calcium oxide may also be excluded because such a mechanism, where both reactants are adsorbed with dissociation and where surface chemical reaction controls the over-all rate, seems incomprehensible for the exchange reaction of atoms. As far as mechanisms I–A, B are concerned we can not determine the values of a, b and c, uniquely. However, in contrast to mechanisms group IV, mechanisms of group I, where only molecular adsorption occurs, may also be improbable for exchange reaction of atoms. Thus mechanisms II–A, B and IV–A, B remain as acceptable.

From preliminary experiments where we measured changes of R with temperature by calcium oxide catalyst to find adequate range of temperature for further resarches, we obtained activation energy of 30.6 kcal./mol. between 697°C and 740°C. In this respect mechanisms II–A, B are most comprehensible. We could not find adequate data concerning adsorption of oxygen or water vapor by calcium oxide. The equilibrium data[5] of dissociation of CaO_2 and $Ca(OH)_2$ give heat of dissociation of 4–11 kcal./mol. for CaO_2 and 25–43 kcal./mol. for $Ca(OH)_2$. Heat of activation must be greater than these and the mechanisms IV–A, B seem more improbable than mechanisms II–A, B. Values of K_o and K_w of mechanisms II–A, B seem reasonable. For these mechanisms K_o is equal to $c_O^2/p_o c_l^2$ and K_w is equal to $c_{H_2O}/p_w c_l$. Then $c_{H_2O}/c_O = p_w K_w/\sqrt{p_o K_o}$. The evaluated values of c_{H_2O}/c_O at $p_o = p_w = 1/2$ are 0.26 for 743°C and 0.57 for 700°C for calcium oxide catalyst and 0.037 for chromic oxide catalyst. Thus the remarkable difference between calcium oxide catalyst and chromic oxide catalyst is the much stronger adsorption of water by the former.

In an earlier paper[6] dealing with exchange reaction of oxygen atoms between gaseous oxygen and water vapor by oxide catalysts of metals belonging to the even series of the first long period of the periodic table of elements we concluded that the exchange reaction catalyzed by calcium oxide would be controlled by adsorption or desorption of water vapor. This conclusion seems inconsistent with the present results. However, earlier researches were done under much lower temperatures than those of the present, and the relative dominating effect of adsorption of oxygen and water vapor for the rate may differ by temperature as can be seen by the great difference of the heat of adsorption between oxygen and water. It can be expected that the rate of adsorption or desorption of water will become the controlling factor in the over-all rate of the exchange reaction by minimizing the concentration of water vapor, i. e. by greater values of α, much more than has been done in these experiments.

Summary

Employing a high-feed rate of reacting gaseous reactants where the rate of reaction did not depend upon the feed rate, measurements of the dependence of the exchange reaction rate of oxygen atoms between gaseous oxygen and water vapor catalyzed by calcium oxide on the mixing molar ratio of reacting gases were made, and the results analyzed by the method of Hougen. The most probable among twenty postulated mechanisms is mechanism II–A where oxygen is adsorbed with dissociation and the rate of dissociative adsorption of oxygen is rate-controlling or II–B where oxygen is adsorbed with dissociation and the recombination of adsorbed oxygen atoms to desorption is rate-controlling. According to these mechanisms, the activation energy of adsorption of oxygen with dissociation or recombination to desorption is about 33 kcal./mol., which is in good agreement with the activation energy 30.6 kcal./mol. for the over-all rate of exchange reaction.

This conclusion is compared to the results obtained with chromic oxide catalyst. The result which was described in an earlier paper is also discussed.

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[5] "International Critical Tables", Vol. VII, p. 294 (1930).

[6] N. Morita, H. Tanaka and T. Titani, This Bulletin, 14, 9 (1939).