Catalysis of H₂–D₂ Equilibration by the O₂-Doped Ag/K System

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Metallic K does not enhance the rate of H_2–D_2 equilibration over Ag, but a very large promoting effect is found if the Ag is first covered with O_2 and then contacted with K. The results of experiments performed in the absence of Ag suggest that this effect is due to an activation of potassium with oxygen.

INTRODUCTION

Metal catalysts promoted by an alkali compound have been used for a long time in, for example, the ammonia synthesis (1) and the Fischer–Tropsch process (2). Although studied profoundly by several researches, this promoting effect is not yet fully understood. Even the nature of the alkali compound in the catalyst is still a subject of research (1e).

Recently a number of studies have been reported in which an alkali metal was used as a promoter (3). Intercalates of alkali metals in graphite have been found to catalyze hydrocarbon reactions (4), and alkali-metal-promoted, supported catalysts have proved active as catalysts for the synthesis of ammonia (3a). Active carbon with an alkali absorbed onto it has been found readily to exchange H_2 and D_2 (5).

It has been reported (6) that even Ag can be activated by an alkali metal to catalyze H_2–D_2 exchange at room temperature and also hydrocarbon reactions.

Since neither Ag nor K catalyze H_2–D_2 exchange to any appreciable extent at room temperature, the catalytic activity displayed by Ag and K when in direct contact with each other can only be related to a change in electronic structure. Since this is a unique situation in metal catalysis, we have decided to examine the Ag/K system more closely.

Ichikawa et al. (6a) studied the Ag/K system using a background pressure of 10^{-4} Torr (1.33×10^{-2} Pa). However, in view of the high sensitivity of K and Ag to oxygen and other impurities, it would seem essential to determine the catalytic activity of the Ag/K system in an apparatus where any effects resulting from gas phase impurities can be excluded. Therefore, we have studied the H_2–D_2 equilibration over Ag/K films in an ultrahigh vacuum (UHV) apparatus which could be evacuated to 10^{-10} Torr. Special attention has been paid to the catalytic activity of the Ag/K films in the presence and absence of O_2.

EXPERIMENTAL

A diagram of the UHV apparatus is shown in Fig. 1. All the valves used were bakable (Granville Phillips). The gas inlet system and the four pumps (1, 3, 4, and 5 in Fig. 1) were placed below, and the Pyrex reaction cell (11) and mass spectrometer (13, Micro Mass; 6, vacuum generators) together with the pressure trans-
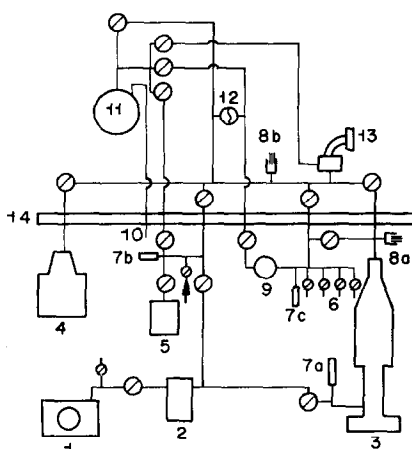
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FIG. 1. The ultrahigh vacuum apparatus. 1, rotary oil pump; 2, molecular sieves; 3, oil diffusion pump; 4, "Vacion" pump; 5, sorption pump; 6, gas inlet system; 7a–c, Pirani vacuum gauges (LKB Autovac); 8a and b, Alpert ionization pressure gauge; 9, potassium bulb; 10, potassium ampoule; 11, reaction cell; 12, Barotron; 13, mass spectrometer; 14, Sindanio table.

ducer (Barotron; range, 10^{-4}–10 Torr) were placed above the (Sindanio) table (14). The system was bakable to 300°C and could be evacuated to 10^{-10} Torr

Three gas bulbs containing ultrapure D_2, Xe (Messer Griesheim GMBR, industrial grades), and ultrapure O_2 (L'Air Liquide) were attached to the gas inlet system (6). H_2 entered the system after diffusion through a heated Ni tube. Before being admitted to the cell (11), H_2, D_2, and Xe could be purified by contacting them with a potassium film (9).

The reaction cell had a volume of about 1000 ml and a geometric surface area of approximately 500 cm². By means of several valves the cell was connected to the gas-dosing system, the UHV apparatus, and the mass spectrometer.

After degassing and melting into a drop, the silver was evaporated from a tantalum filament onto the wall of the reaction cell (Fig. 2). Sometimes a second filament of tungsten was also present in order to atomize H_2.

Using a set-up different from that shown in Fig. 2, we have performed experiments with a Ag film in the absence of filaments (Fig. 3). In this set-up the filaments could be maneuvered with the aid of bellows so that the Ag could be evaporated into the cell, and after evaporation the tantalum could be withdrawn from the cell by disconnecting the bulb with bellows from the cell by melting the glass connections, without increasing the pressure in the cell above 10^{-8} Torr.

The potassium metal (Alfa Europe Products; purity, $\geq 99.9\%$) was distilled under UHV conditions ($<10^{-7}$ Torr) at 275°C from the ampoule in which it had been supplied into smaller ampoules which could be attached to the reaction cell. The potassium-containing part of the glass tube connecting the ampoule with the reaction cell was placed just under the Sindanio table by fitting it through a hole in this table. In this way the reaction cell could be baked after attaching the potassium ampoule to it.

Potassium could be evaporated into the reaction cell by breaking the seal and heating the potassium ampoule with a flame or by placing the reaction cell with
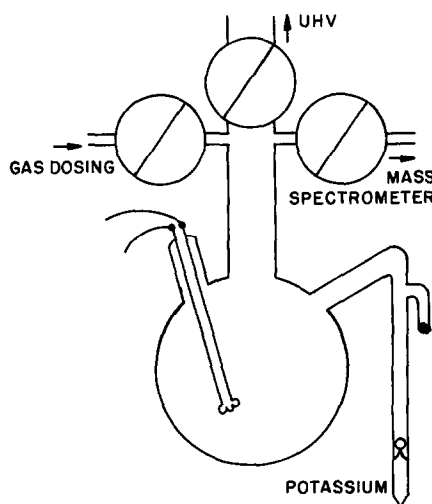

FIG. 2. Reaction cell.

the potassium-containing side arm into a thermostatted oil bath (maximum bath temperature, 200°C). The dimensions of the reaction cell and ampoule had been chosen such that they could be placed in a Dewar flask.

ANALYSIS OF THE KINETIC DATA

All the kinetic measurements were performed at room temperature. A mixture of approximately equal amounts of hydrogen and deuterium with a total pressure of 0.1 Torr (13.3 Pa) was contacted with the film. The ratio P,

$$P = [HD]/([H_2][D_2])^{\frac{1}{2}}, \quad (1)$$

was measured as a function of time by the mass spectrometer.

If one assumes that formation of HD occurs according to the following equation,

$$d[HD]/dt = k[H_2][D_2] - (K/k)[HD]^2, \quad (2)$$

then $[HD] = z$ is the solution of the differential equation:

$$dz/dt = k\{z^+ - z)(z^- - z)\}, \quad (3)$$

where

$$z^{\pm} = \{\tfrac{1}{2}(a + b) \pm [\tfrac{1}{4}(a - b)^2 + 4abK]^{\frac{1}{2}}\}/ \\ 2(\tfrac{1}{4} - K); \quad (4)$$

K is the equilibrium constant, which at 23°C has a value of 0.31; and a and b are

FIG. 3. Reaction cell with movable filaments.

TABLE 1

Effect of Potassium on H₂-D₂ Equilibration Rate Constant over Silver

	k (10^{-8} Pa^{-1} s^{-1})	
Ag	6.7	5.4
Ag + K	5.6	1.8

the initial concentrations of H_2 and D_2, respectively. The solution of Eq. (2) has the form:

$$(z - z^+)/(z - z^-) = (z^+/z^-)e^{\alpha t}, \quad (5)$$

with

$$\alpha = k(z^+ - z^-). \quad (6)$$

If

$$R = (z^-/z^+)([z - z^+]/[z - z^-]), \quad (7)$$

then a plot of $\ln R$ as a function of time should be a straight line of slope α. In the general case where $a \neq b$, R becomes a rather elaborate function of $P(t)$. We have used this expression of R and found usually very good agreement with Eq. (5). Thus, once α had been determined, k could be calculated from Eq. (6).

RESULTS

Table 1 gives the k values derived from two experiments performed in the absence of oxygen. At 175°C potassium was distilled onto the silver for only 5 min, after which the surface coverage θ_k was ~0.7. This θ_k value was obtained by comparing the amounts of H_2 desorbed from the Ag film, which had been presintered at 200°C, before and after potassium distillation.

The hydrogen was adsorbed by atomization of H_2 gas at 0.1 Torr using a tungsten filament at $-210°C$. H_2 molecules desorb at approximately $-83°C$ from Ag, whereas the surface layer of potassium hydride does not start to decompose even at room temperature.

From Table 1 it is seen that the equilibration rate had decreased after potassium admission.
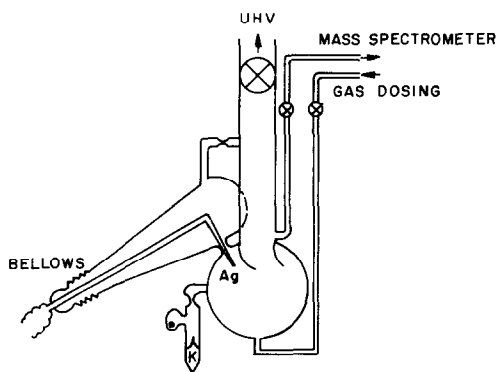
TABLE 2

Effect of Oxygen H$_2$–D$_2$ Equilibration
Rate Constants over Silver

	k (10^{-8} Pa^{-1} s^{-1})	
Blank	6.5	—
Blank + O$_2$	5.6	—
Ag	3.8	3.2
Ag + O$_2$	2.3	1.6
Ag+O$_2$+K	21.4	11.5
After 16 hr	69.5	65.9

The results of two experiments performed in the presence of small amounts of oxygen are presented in Table 2. This table shows that preadsorption of oxygen onto the silver (in an amount of the order of a monolayer) decreases the equilibration rate, but that subsequent admission of a few monolayers of potassium induces a great enhancement, which increases with time.

However, to find out whether this enhancement was due to promotion of potassium by oxygen, we decided to study the effect of oxygen on a pure potassium film. The results are summarized in Table 3. In this table Q_t represents the total amount of O$_2$ added (moles) per mole of K (determined afterwards by atomic absorption) present in the reaction cell. Very great enhancements, increasing with time, were found. At $Q_t = 2 \times 10^{-3}$, the color of the potassium film changed from metallic to blue, probably the color of potassium suboxide, and started absorbing hydrogen.

TABLE 3

Effect of Oxygen on H$_2$–D$_2$ Equilibration
Rate Constants over Potassium

	k (10^{-8} Pa^{-1} s^{-1})
Blank	3.5
K	5.3
+O$_2$ ($Q_t = 4 \times 10^{-5}$)	6.1
+O$_2$ ($Q_t = 10^{-4}$)	11.4
after 27 hr	30
+O$_2$ ($Q_t = 6 \times 10^{-4}$)	51
+O$_2$ ($Q_t = 2 \times 10^{-3}$)	353
+O$_2$ ($Q_t = 3 \times 10^{-2}$)	338
+O$_2$ ($Q_t = 10^{-1}$)	1.4

The amount of hydrogen ultimately absorbed was approximately equal to the amount of oxygen added to the potassium. At $Q_t = 0.1$ the blue color of the film had vanished and the film became inactive.

Table 4 presents the results of two experiments in which the potassium had been exposed to atomic hydrogen. It shows that the rate of equilibration, which was very low over potassium, was greatly enhanced upon preadsorption of hydrogen atoms.

DISCUSSION AND CONCLUSION

Recently Hayashi *et al.* (*6c*) have reported new results of an investigation into the catalytic activity of alkali-metal group IB metal alloys in a closed circulation system. Their results are comparable to those previously found by Ichikawa *et al.* (*6a*). However, they found an enhancement in activity that was several orders of magnitude larger than that observed by us. It is probable that this difference arises from the heat treatments they gave to their catalysts. Our films were not subjected to such heat treatments.

Our experimental results clearly indicate the absence of a promoting effect of potassium metal on silver and the existence of a pronounced promoting effect of oxygen on potassium. The latter effect is observed both in the presence and in the absence of Ag. The result of the experiment in which prior to potassium deposition oxygen had been adsorbed onto the silver (Table 2) can be rationalized, if one assumes that the potassium reacts with the oxygen preadsorbed onto the Ag to form a suboxide. This has indeed been observed by others (*7*). The promoting activity of oxygen on potassium reaches a maximum when the film turns blue. Suboxides of Cs (*8*) and Na (*9*) are brown (black) and bluish black, respectively. Potassium peroxides and superperoxides are orange and orange-yellow. Potassium oxide is yellowish-white (*10*). It is therefore most likely that the blue-colored potassium compound is some combination of potassium and potassium oxide,

TABLE 4

Effect of Atomic Hydrogen on H_2–D_2 Equilibration Rate Constants over Potassium

	k $(10^{-8}$ Pa^{-1} s$^{-1})$	
Blank	0.9	1.2
K	3.2	14.5
K + H	54.5	92

in which the charge on the oxygen atom is closer to 1 than to 2. The experiment with potassium indicates that there is a decline in activity when too much O_2 is present and the blue color vanishes; probably some mixture of K_2O and KOH is formed. This suggests that small clusters of potassium atoms near an oxygen atom are needed for the oxygen-doped potassium film to be active.

The experiments with atomized hydrogen show that the rate of equilibration over potassium is greatly enhanced upon pre-adsorption of hydrogen atoms. Hence, the dissociation of H_2 and D_2 molecules is rate limiting, but once atomic hydrogen is adsorbed, rapid equilibrium is possible probably proceeding via a Rideal-type mechanism:
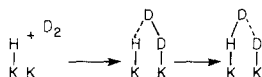
Alkali oxides readily form hydroxides and alkali hydrides with H_2 (10):

$$K_2O + H_2 \rightarrow KOH + KH. \qquad (8)$$

We therefore tentatively propose the following mechanism to explain the promotion of alkali metal by oxygen:

(I) A suboxide is formed, which in turn catalyzes the formation of KH [see Eq. (8)].

(II) Equilibration proceeds via Rideal-type mechanism, requiring an empty site next to an adsorbed hydrogen atom. Therefore, the equilibration reaction will not be catalyzed when the initial oxygen uptake is too large.

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