JOURNAL OF CATALYSIS 25, 194–203 (1972)

Catalytic Oxidation of Ethanol Over Tantalum Oxide

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Received April 30, 1971

The reaction of ethanol and oxygen on tantalum oxide has been investigated at 250–320°C. In the early stages of the reaction, the catalyst activity is rather low and ethanol undergoes dehydration as well as oxidation. However use of the catalyst for a long period causes a remarkable increase in the rate of acetaldehyde formation. The kinetics of the oxidation on an active catalyst have been studied in a differential reactor. A mechanism is proposed that satisfactorily explains the reaction orders and the inhibiting effect of water.

INTRODUCTION

The possibility of obtaining aldehydes by oxidation of primary alcohols on solid catalysts has been investigated in few cases. More often aldehydes are obtained by dehydrogenation of primary alcohols on metal catalysts such as nickel (*1*) and copper. Only in the case of methanol has the process of oxidation by oxygen received much attention. For instance, on catalysts such as MoO_3, V_2O_5 and related oxides, the oxidation of methanol to formaldehyde proceeds with a very high degree of selectivity (*2, 3*).

On the other hand the reaction of other primary alcohols and particularly ethanol on various oxide catalysts has been examined from the point of view of selectivity (*4*). These experiments were carried out in the absence of oxygen so that aldehyde apparently resulted from a dehydrogenation as well as from an oxidation process. Thus it seemed desirable to examine the conversion of ethanol on an oxide catalyst, under oxidative or reductive conditions, in order to separate the two processes.

The oxide chosen for this investigation was tantalum pentoxide. Ta_2O_5 is employed in the catalytic production of butadiene from ethanol and acetaldehyde. The mechanism of this condensation has been investigated in detail by Quattlebaum, Toussaint, and Dunn (*5*). In their study the silica gel catalyst was promoted with other oxides, among which tantalum oxide seems particularly effective. The first step of the reaction is the conversion of acetaldehyde into crotonaldehyde; the intermediate crotonaldehyde is rapidly deoxygenated into butadiene by means of ethanol.

$$CH_3{-}CH{=}CH{-}CHO + C_2H_5OH \rightarrow CH_2{=}CH{-}CH{=}CH_2 + CH_3CHO + H_2O$$

According to these authors, the addition of tantalum oxide to the silica catalyst has two effects; it accelerates the condensation of acetaldehyde into crotonaldehyde, and also the conversion of crotonaldehyde into butadiene by ethanol. Since this latter reaction involves a hydrogen transfer between adsorbed alcohol and crotonaldehyde, tantalum oxide behaves as an oxidation–reduction catalyst. However, the interaction between crotonaldehyde and ethanol is probably not a simple process, and if we want to obtain general information on the catalytic properties of Ta_2O_5, it is better to study first the conversion of ethanol on this oxide. Thus it was decided to investigate in detail the interaction of ethanol and pure tantalum oxide. Since, in the conditions of the butadiene synthesis, the conversion of ethanol into acetaldehyde is apparently slow, it seemed advantageous to study the

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reaction of ethanol in the presence of oxygen. The aim of the present paper is to indicate the kinetic aspect of the reaction, and to draw some conclusions about possible mechanisms.

EXPERIMENTAL

Apparatus

The experiments were performed in a flow apparatus, generally under differential conditions. Reaction rates were determined as a function of oxygen and ethanol partial pressures in the temperature range 150–340°C, the total pressure being one atmosphere.

The apparatus was fed with oxygen and nitrogen from two cylinders. Flow rates were stabilized through precision manometers, and measured by capillary flow meters (Prolabo). After dehydration over zeolite 3A, the carrier gas entered a vaporizer. Two types of vaporizer were used. In the first type, designed to provide low partial pressures of ethanol, liquid alcohol was absorbed in Chromosorb. The vaporizer was placed in a constant temperature bath: we ensured that at all flow rates the ethanol partial pressure of the exit gas was exactly equal to its vapor pressure at the temperature of the bath. In the second type of vaporizer, liquid alcohol was continuously fed from a syringe driven at a constant velocity by a motor system equipped with interchangeable gears, and then vaporized in a heated glass spiral.

The reactor was a quartz tube, 10 mm in diameter, equipped with a thermocouple well (Pyrex glass proved unsatisfactory as a material for the reactor). Usually, the reactor contained one gram of undiluted tantalum oxide.

Reaction products were taken at the reactor exit either in the gas phase or after condensation in a collecting bath kept at −127°C.

Products

Tantalum oxide Ta_2O_5 (99.9% purity) was provided by Koch-Light as a fine microcrystalline powder. According to X-ray analysis the crystals belonged to the orthorhombic β phase. No change in the X-ray spectrum was noticed after prolonged use. The surface area, measured by nitrogen adsorption at 77°K, was 1.20 m^2/g; the average grain size was around 20 μ.

Acetaldehyde and ethanol were R.P. products from Prolabo. Ethanol was carefully dried prior to use. The purity of oxygen and nitrogen gases (Air Liquide) was checked by mass spectrometry. Typically, nitrogen (R. quality) contained 0.13% oxygen.

Analyses

Reaction products were collected at the reactor exit either in the gas phase or after condensation in a cold trap, and analyzed by gas chromatography. The detector was a flame ionization head; a 3 m column impregnated with cyanosilicone (XF 1150) ensured a complete separation of ethylene, ether, butadiene, acetaldehyde and ethanol. In some special analyses of the light products, dimethylsulfolane or silica columns were used. Conversion degrees x were expressed as the fraction of reacted ethanol.

RESULTS

Nature of the Reaction Products

When a fresh sample of tantalum oxide was placed in the reactor and subjected to an ethanol–oxygen mixture, a reaction was observed at about 300°C. Three main products were formed: ethylene, ethyl ether and acetaldehyde. Figure 1 shows the product distribution as a function of $(1/F)$ (F = flow rate of gaseous ethanol expressed in moles per hour) in an experiment at 315°C. The above three products appeared from the start. Butadiene was formed as a secondary product, appearing as the conversion into acetaldehyde exceeded 5%.

Traces of propylene, butene and carbon dioxide were also noticed. On this fresh catalyst, the following apparent activation energies were measured in the temperature range 290–340°C.

For the formation of acetaldehyde: E = 26.6 kcal/mole

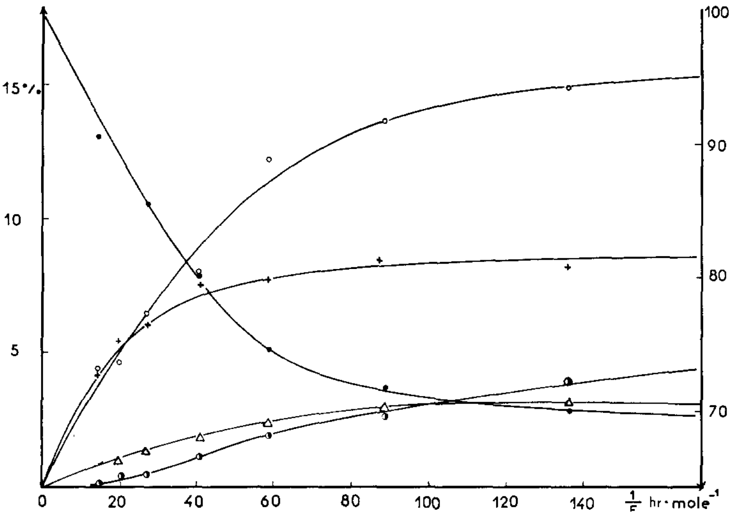


FIG. 1. Product distribution as a function of contact time for 1 g of fresh Ta_2O_5. Temperature 315°C; ethanol initial pressure P_A = 42.5 Torr; oxygen initial pressure P_O = 717 Torr: ● ethanol, ○ ether; + acetaldehyde; △ ethylene; ◑ 1,3-butadiene.

For the dehydration into ethylene: E = 20.7 kcal/mole

For the dehydration into ether: E = 21 kcal/mole

Catalyst Selectivity and Ageing

If the ethanol–oxygen feed is maintained on the catalyst for a long period, a change in the distribution of the reaction products is observed after several hours. The rate of oxidation into acetaldehyde increases continuously with time while dehydration reactions are little affected. Table 1 shows the pattern of the main reaction products obtained at 290°C on a fresh sample (1 g) of Ta_2O_5 (first row), then on the same sample after one day of continuous operation (second row). The catalyst can be stabilized at this stage after treatment with ethanol vapor at 350°C in a closed receiver. Otherwise, the catalytic activity of the tantalum oxide steadily increases. The final stage of activation, shown in the third row of Table 1, yields a very selective catalyst; the rate of oxidation into acetaldehyde is so much increased that this reaction occurs at 200°C and can still be detected at 150°C.

Active Catalyst: Temperature Effect

In its final state of activation tantalum oxide exhibits a remarkable selectivity for the oxidation of ethanol into acetaldehyde. A study of the other reaction products has been made at various temperatures, the flow rate and feed composition being kept constant. The percentages of the different products are indicated in Fig. 2. At the lowest temperature, the main byproducts are ethylene and methyl acetate. A rise in

TABLE 1

CONVERSION OF ETHANOL AT 290°C ON ONE GRAM OF Ta_2O_5[a]

	Acetaldehyde (%)	Ether (%)	Ethylene (%)	Butadiene (%)
Fresh catalyst	0.6	0.75	0.20	0.1
Catalyst after 1 day (stabilized)	9	0.9	0.80	0.6
Catalyst after 7 days of operation	50	0.5	1.50	0.8

[a] Measurements performed at P_A/P_O = 0.0705; ethanol flow rate F = 0.0107 mole hr^{-1}.

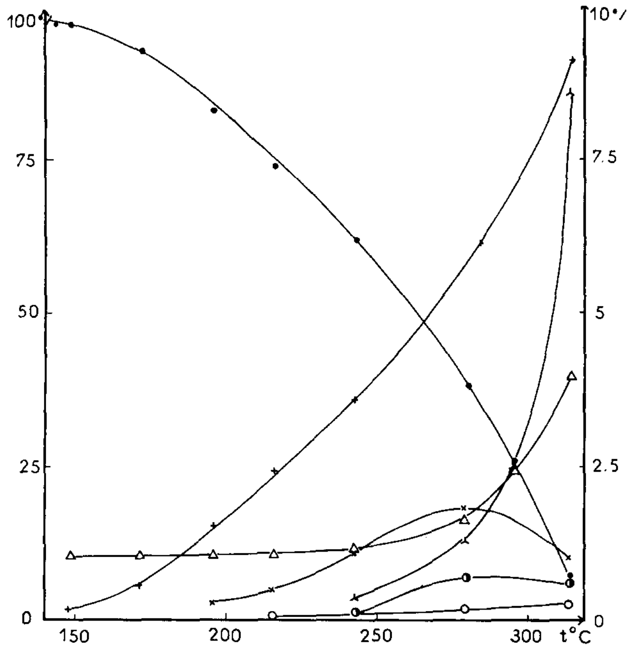


FIG. 2. Product distribution as a function of temperature for 1 g of activated Ta_2O_5 — $P_A = 50$ Torr; $P_0 = 710$ Torr; ethanol flow rate $F = 0.851\ 10^{-3}$ mole hr^{-1}. Left scale (0–100%): ● ethanol; + acetaldehyde. Right scale (0–10%): ○ ether; ◑ butadiene; ⅄ (methanol + ethyl acetate); × methyl acetate; △ ethylene.

temperature to 250°C produces some ether, the concentration of which remains extremely low, butadiene, methanol, methane and ethyl acetate. It seems that the formation of butadiene is greatest at about 300°C; this is consistent with the fact that ethanol is involved in the formation of butadiene, presumably by means of a reduction of crotonaldehyde, since the final concentration of ethanol remains very small above 300°C.

In any case, the concentration of crotonaldehyde in the gas phase is low, as in the case of the synthesis of butadiene (*5*). Only slight traces of crotonaldehyde (less than 0.5%) are found at 300°C.

Thus, on the active tantalum oxide the product distribution is somewhat different from the one obtained on a fresh catalyst. In the low temperature region (150–210°C) an activation energy of 20 kcal/mole is found in the case of the oxidation into acetaldehyde. The activation energy is noticeably lower on an active than on a fresh catalyst, but it is interesting to note that total oxidation into carbon dioxide is not favored by the activation process: the amounts of CO and CO_2 are always much smaller than the amount of ethylene formed in the same conditions.

Kinetic Study: Orders of Reaction

Since on an active sample of Ta_2O_5 the oxidation into acetaldehyde occurs with a selectivity of at least 90% at 300°C, a kinetic study of the reaction was carried out. It was first ascertained that the percent conversion into acetaldehyde, x, did not vary when the ratio W/F was kept constant at a given temperature: the catalyst mass W varied from 1.4 to 10 g. Thus diffusion effects are unimportant in our experimental conditions. Then it was found that the reaction forms equal quantities of water and acetaldehyde. Hence the stoichiometry is

$$C_2H_5OH + \tfrac{1}{2}O_2 \rightarrow CH_3CHO + H_2O$$

With the reactor working in differential conditions, a preliminary study of the variation of the reaction rate with the concentration of each reactant was undertaken.

Figure 3 shows the rate of ethanol oxidation as a function of oxygen pressure at 300°C. the ethanol pressure being fixed at 52 Torr. The reaction order decreases from 0.40 to 0.20 as the oxygen pressure rises from 2 to 710 Torr. Figure 3 also shows the variation of the rate of oxidation as a function of the ethanol partial pressure at the same temperature 300°C, the oxygen pressure being fixed at 235 Torr. The reaction order for ethanol varies from 0.46 to 0.26 as the ethanol partial pressure increases from 34 to 352 Torr. Experiments conducted with still lower ethanol pressures showed that the reaction order never exceeded 0.5.

Addition of water vapor to the feed caused a marked decrease in the rate of oxidation. Figure 4 shows the results obtained at 300°C: in each experiment, the ethanol and oxygen pressures are kept constant, and the rate r is plotted as a function of P_{H_2O}. It can be observed that the decrease in the rate is less pronounced at higher alcohol pressures.

Addition of acetaldehyde to the entering reaction mixture also caused a decrease in the rate of oxidation, roughly similar to the effect of water.

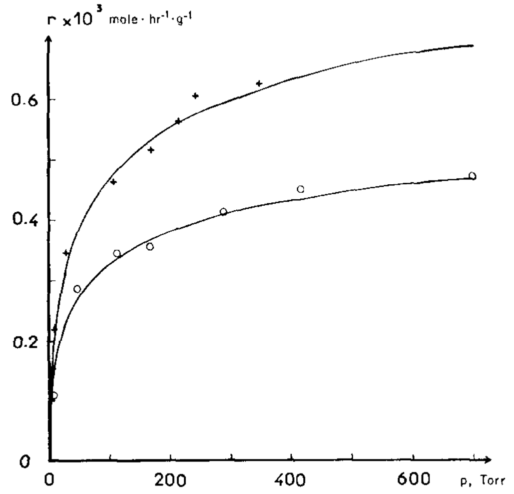


FIG. 3. Initial reaction rate as a function of reactant partial pressure for 1 g of activated Ta_2O_5. Temperature 300°C. + measurements at P_A variable and P_o constant (P_o = 235 Torr); ○ measurements at P_o variable and P_A constant (P_A = 52 Torr). Curves are calculated according to Eq. (5).

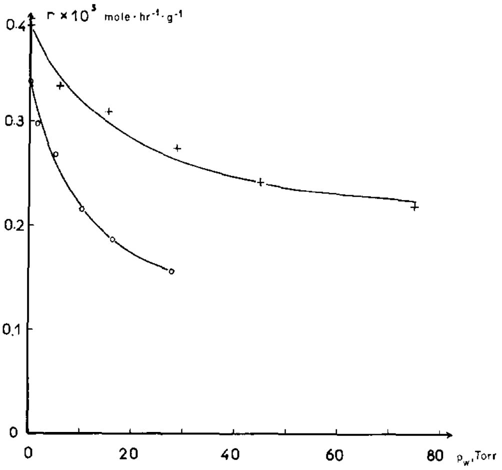


FIG. 4. Initial reaction rate as a function of water pressure for 1 g of activated Ta_2O_5. Temperature 300°C. ○ P_o = 720 Torr; P_A = 30 ± 2 Torr; + P_o = 650 Torr; P_A = 82 ± 6 Torr.

Kinetic Analysis

The above results suggest that the rate of oxidation is not governed by the adsorption of one of the reactants. Similarly a reaction between alcohol from the gas phase and oxygen adsorbed on the surface could not account for the results observed. In order to establish a satisfactory rate equation, measurements of r were carried out at 300°C on a catalyst of constant activity and at a low conversion rate, varying systematically the partial pressures of the two reactants. The results of 44 such measurements were then treated by regression methods on the basis of a large number of possible rate equations. The following cases were considered to be rate determining:

I. Adsorption of one reactant

II. Reaction between adsorbed oxygen and gas phase alcohol

III. Steady state adsorption model, according to Mars and Van Krevelen: competition is assumed between the adsorption of oxygen and the removal of adsorbed oxygen by a gas phase organic molecule (*6*).

IV. A steady-state adsorption model involving three steps as suggested by Mann and Hahn (*7*).

V. A surface reaction (Langmuir mechanism) in which it is assumed that both reactants are adsorbed on the same type of sites.

VI. A surface reaction (Langmuir) in which it is assumed that both reactants are adsorbed on two different types of sites.

The rate equations corresponding to each mechanism are given in Table 2: for each mechanism different values of the numbers *m* and *n* were tried.

Equations of the types I, II and III containing two parameters were linearized. Using the experimental results, the parameters *k* and *K* were calculated by the least-squares method (linear regression). Table 2 shows that, although the parameters of the correct sign were found, the square of the linear correlation coefficient ρ^2 is rather low, except for mechanism III (Mars and Van Krevelen) with *m* (reaction order versus ethanol) equal to 0.5.

Equations of the types IV and V, containing three parameters, were similarly linearized and the parameter values calculated by three dimensional linear regression. The square multiple correlation coefficients ρ^2 (Table 2) are rather good, particularly for case V; but the negative values found for some of the *K* parameters in case IV permit us to reject the corresponding mechanisms.

Since equations of type VI could not be linearized with three variables, the next step was to treat them by a method of nonlinear regression, together with equations III, IVa and V which proved to be more satisfactory on the basis of the linear regression. The grid search method (*8*) which was employed consisted of minimizing the sum $Q_{(k)}$ of the squares of deviations for the reaction rates. Given an initial choice of the parameters *k* and *K* (those found by linear regression or, in case VI, derived from curves 3), systematic variations were given to these parameters in order to lower the *Q* value.

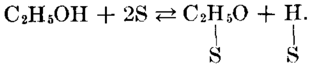
This iteration usually converged on a new set of *k* and *K* corresponding to the true minimum of the function $Q_{(k)}$. The final *Q* values are given in Table 2 for each type of equation. One advantage of this method is that all of the equations may be compared with the same criterion, i.e., the value of the quantity *Q*, whereas the ρ^2 coefficient in the linear regression correlates variables that are not similar for the different equations tested. Clearly, the $Q_{(k)}$ values for mechanisms Vd and VId are the lowest.

For each of these mechanisms, the parameters *k* and *K* corresponding to the minimal values of *Q* ($Q = 7.96 \times 10^{-6}$ and 7.73×10^{-6}, respectively) are considered as the most probable ones. However, the confidence limits of the parameters can be fixed by considering the critical value of the sum of squares of deviations. Using the formula given by Beale (*9*) we estimate that, on a 95% significance level, the correct parameters for equation Vd and VId are those which give $Q_{(k)}$ values smaller than 9.8×10^{-6} or 9.51×10^{-6}, respectively. Moreover, following the arguments of Beranek (*8*) we exclude from further consideration any equation other than Vd and VId since all of them give $Q_{(k)}$ values much higher than the critical value for equation VId.

Mechanism of the Reaction

From the formal kinetic analysis of the oxidation on the activated catalyst, it follows that the rate-determining step is a surface reaction between adsorbed ethanol and adsorbed oxygen. Although two possibilities for the adsorption of reactants seemed to correlate the rate measurements equally well, it is hardly possible from a mechanistic point of view to consider that the two reactants, ethanol and oxygen, be adsorbed by the same type of site on the tantalum oxide surface (equation type V).

A possible mechanism involving adsorption of both reactants by two separate sets of sites may be proposed in the following manner. First, one ethanol molecule is assumed to undergo dissociative adsorption on two sites S



$$C_2H_5OH + 2S \rightleftarrows \underset{\displaystyle S}{\underset{|}{C_2H_5O}} + \underset{\displaystyle S}{\underset{|}{H}}. \qquad (1)$$

TABLE 2
SUMMARY OF KINETIC MODELS TESTED[a]

Type of mechanism	Rate equation	Tested parameters and orders	Sign of computed K[b]	ρ^2 (linear regression)	$Q(k) \times 10^6$ (grid search) (mole hr^{-1} g^{-1})^2
I	$r = \frac{kP_A}{[1 + (K_OP_O)^n]^\alpha}$	a) $\alpha = 1$ and $n = 1$	+	0.03	[c]
		b) $\alpha = 2$ and $n = 1$	+	0.01	[c]
		c) $\alpha = 1$ and $n = 0.5$	+	0.06	[c]
		d) $\alpha = 2$ and $n = 0.5$	+	0.02	[c]
II	$r = \frac{kP_A(K_OP_O)^n}{1 + (K_OP_O)^n}$	a) $n = 1$	+	0.54	[c]
		b) $n = 0.5$	+	0.36	[c]
III	$r = \frac{k_Ak_OP_A{}^mP_O{}^n}{0.5k_AP_A{}^m + k_OP_O{}^n}$	a) $m = 1$ and $n = 1$	+	0.47	169
		b) $m = 0.5$ and $n = 1$	+	0.88	21.3
		c) $m = 1$ and $n = 0.5$	+	0.60	40.4
		d) $m = 0.5$ and $n = 0.5$	+	0.80	17.5
IV	$r = \frac{k_Ak_OP_A{}^mP_O{}^n}{0.5k_AP_A{}^m + k_OP_O{}^n + \frac{k_Ak_O}{k}P_A{}^mP_O{}^n}$	a) $m = 1$ and $n = 1$	+	0.80	76.6
		b) $m = 0.5$ and $n = 1$	−	0.81	[c]
		c) $m = 1$ and $n = 0.5$	−	0.87	[c]
		d) $m = 0.5$ and $n = 0.5$	−	0.87	[c]
V	$r = \frac{kK_AK_OP_A{}^mP_O{}^n}{(1 + K_AP_A{}^m + K_OP_O{}^n)^2}$	a) $m = 1$ and $n = 1$	+	0.93	154
		b) $m = 0.5$ and $n = 1$	+	0.90	148
		c) $m = 1$ and $n = 0.5$	+	0.90	64
		d) $m = 0.5$ and $n = 0.5$	+	0.92	7.96
VI	$r = \frac{kK_AK_OP_A{}^mP_O{}^n}{(1 + K_AP_A{}^m)(1 + K_OP_O{}^n)}$	a) $m = 1$ and $n = 1$		[c]	34
		b) $m = 0.5$ and $n = 1$		[c]	14.6
		c) $m = 1$ and $n = 0.5$		[c]	21.9
		d) $m = 0.5$ and $n = 0.5$		[c]	7.73

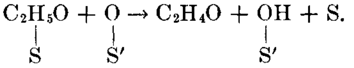
[a] k = rate constant; K_A, K_O: adsorption coefficients; k_A, k_O: adsorption rates; P_A, P_O: reactants partial pressures (A stands for ethanol, O for oxygen).

[b] + means that all K and k are found positive; − means that this criterion is not satisfied.

[c] Not tested.

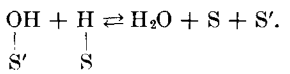
The nature of these sites is not easy to establish at present. If we tentatively identify them with oxide ions, it is difficult to explain on this basis the activation which was observed during the reaction. Alternatively the two sites adsorbing an alcohol molecule may be different in nature, but equal in number.

If oxygen is assumed to adsorb dissociatively on sites S′, (presumably metal ions) the surface reaction may be written thus:



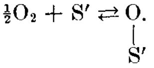
$$\underset{S}{C_2H_5O} + \underset{S'}{O} \rightarrow C_2H_4O + \underset{S'}{OH} + S. \qquad (2)$$

Then adsorbed hydroxyl may be desorbed into water



$$\underset{S'}{OH} + \underset{S}{H} \rightleftarrows H_2O + S + S'. \qquad (3)$$

The reoxidation of sites S′ is simply



$$\tfrac{1}{2}O_2 + S' \rightleftarrows \underset{S'}{O}. \qquad (4)$$

Assuming a Langmuir type adsorption for all gaseous species and calling k_2 the rate constant of Reaction (2), this overall mechanism leads to a simple form of the initial reaction rate in the case where the water pressure is negligible:

$$r = \frac{k_2 K_A^{1/2} P_A^{1/2} K_O P_O^{1/2}}{(1 + K_O P_O^{1/2})(1 + 2K_A^{1/2} P_A^{1/2})}. \qquad (5)$$

The experimental data on reaction rates as a function of oxygen or ethanol partial pressure (Fig. 3) are well represented by this rate equation; for instance, good straight lines are obtained when plotting $P_0^{1/2} r$ vs. $P_0^{1/2}$ at constant P_A.

The rate constant k_2 and the adsorption coefficients K_A and K_0 were determined at three temperatures for a catalyst of approximately constant activity. The results are shown in Table 3: an activation energy of 21.2 kcal/mole^{-1} is then derived for the rate determining surface reaction.

More informative perhaps is the fact that the inhibitory effect of water may be satisfactorily explained by the proposed mechanism. At high oxygen partial pressure (P_0), and at low pressure of ethanol (P_A) and water (P_W), calculations based on Eq. (1)–(4) yield the following expression for the oxidation rate:

$$r = \frac{r_0}{[1 + \mu K_W P_W (K_A P_A)^{-1} (1 + K_o P_o^{1/2})^{-1}]^{1/2}}$$

Here, r_0 is the rate in the absence of water, as given by Eq. (5); K_W is the adsorption coefficient of water [Eq. (3)], and μ is the ratio between the total number of sites (S) and (S′). This expression for the rate of reaction is only approximate, since it is assumed that the concentration of bare sites S is not greatly modified by the presence of water, which is true only for low P_W values.

Nevertheless, the degree of agreement with experiment is rather satisfactory, as may be seen in Fig. 5. From Eq. (6), it may be predicted that at constant oxygen pressure P_0, the ratio r_0^2/r is a linear function of P_W/P_A. The two sets of points in Fig. 5 correspond to experiments with different values of P_A. The linear relationship is well maintained for the lower P_A value (30 Torr). For the higher P_A value (82 Torr) the agreement is not as good when P_W/P_A exceeds 0.3; but then P_W is rather high and the previous simplifications no longer hold.

TABLE 3

RATE CONSTANTS AND ADSORPTION COEFFICIENTS

T°C	300	275	259
k_2 mole h^{-1} g^{-1}	3.07×10^{-3}	1.31×10^{-3}	0.78×10^{-3}
$K_A^{1/2}$ (Torr)$^{-1/2}$	0.0481	0.082	0.104
K_O (Torr)$^{-1/2}$	0.109	0.170	0.246

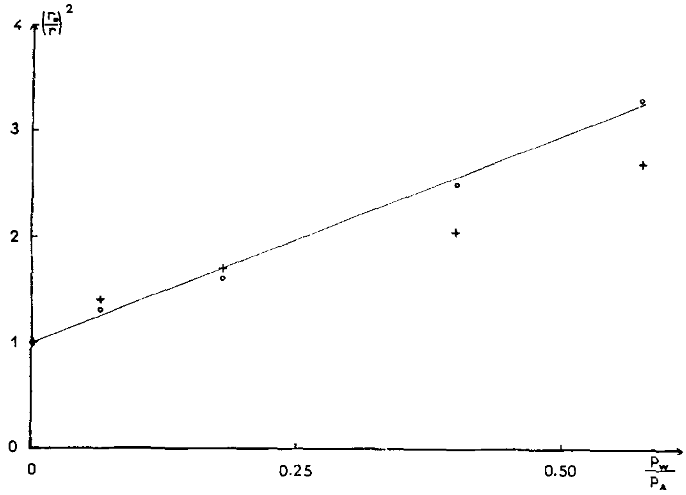


FIG. 5. Effect of water on the initial reaction rate: test of Eq. (6). ○ $P_o = 720$ Torr; $P_A = 30 \pm 2$ Torr; + $P_o = 650$ Torr; $P_A = 82 \pm 6$ Torr.

It should be pointed out that the proposed oxidation mechanism [Eqs. (1)–(4)] is based solely on kinetic arguments. These give only a formal description of the catalytic surface. In a recent work on methanol oxidation over MoO_3–$Fe_2(MoO_4)_3$ catalyst, Pernicone *et al.* (*10*) obtained results somewhat similar to ours. These authors report reaction orders of ½ for both methanol and oxygen, in the low partial pressures region (up to 100 Torr for each reagent). The orders become zero at higher pressures. Moreover, the same authors report that water has a marked inhibitor effect on the reaction rate. They assume that the adsorption of methanol occurs dissociatively on a pair of acid–base sites of the surface. Although we do not want to discuss fully the nature of the adsorption sites in our case, it would be tempting to adopt such a model for the adsorption of ethanol on tantalum oxide. But a major difficulty is met in connection with the activation of the catalyst upon ageing. If alcohol adsorption occurs as on the molybdenum catalyst, the activation process would probably be the creation of anionic vacancies on the surface. It is to be expected that such vacancies are created upon high temperature vacuum treatment, but we have observed that the activation of our catalyst did not occur in these conditions; it required the presence of both ethanol and oxygen.

A slightly different model has been proposed by Jiru (*11*) for the adsorption of methanol on pure MoO_3: the site is still a coordinatively unsaturated metallic ion, and a methyl hydrogen is bonded to a surface oxygen. Applying these ideas to our kinetic treatment of ethanol on Ta_2O_5, and supposing different rate-determining steps, we obtained rate expressions (such as IIb or a modification of IV) that did not correctly fit the experimental results. Thus the surface state of tantalum oxide seems more complicated than for the molybdenum catalyst. Moreover, tantalum oxide displays some acidic centers as evidenced by the production of ethylene and ether. Although we do not know the nature and number of these sites, it is clear that the dehydrating and oxidizing power vary in opposite directions according to the catalyst treatment. It may be possible that the sites necessary for alcohol adsorption and oxidation are created during the reaction itself, and are not connected directly with the oxide structure.

The rate-determining surface reaction, as written in Eq. (2), is probably an oversimplification, since it is likely that the acetaldehyde molecule is first produced in an adsorbed state. Indeed, the inhibitory effect noted when a small quantity of acetaldehyde was introduced into the feed shows that the aldehyde may be adsorbed on the surface. In the work quoted above, Pernicone *et al.* arrive at the conclusion that methanal desorption is the slow step of the process of methanol oxidation on the iron molybdenum catalyst in the low temperature region. In the present case, it is unlikely that aldehyde desorption is rate-determining in the range of temperature and pressure investigated. Indeed, if product desorption is substantially faster than the surface reaction, it does not affect the kinetic law.

Finally, not enough details are available to permit discussion of the selectivity of the oxidation in connection with the nature and strength of the metal–oxygen bond in the catalyst. According to data on the isotopic exchange of oxygen with tantalum oxide (*12*), it is reasonable to expect that in this solid the lattice oxygens could participate in an oxidation reaction. But the number of adsorption sites for oxygen on the surface is relatively small: this is to be related to the lower activity of the Ta_2O_5 catalyst compared with the best catalysts used in alcohol oxidation (*13*).

ACKNOWLEDGMENT

We wish to thank Professor L. Beranek (Prague) for fruitful discussions and his help in carrying out the computer calculations.

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