J. Chem. Soc., Faraday Trans. 1, 1981, **77**, 2977-2988

Interaction of Alcohols with Evaporated Metal Films

Part 2.—Adsorption and Decomposition of Ethanol on Metal Films of Nickel, Palladium and Aluminium

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Received 26th November, 1980

The interaction of ethanol with clean and oxidized films of Ni, Pd and Al has been investigated in the temperature range 223-450 K. Dissociative adsorption of ethanol on the clean surfaces took place even at 223 K. Reversible molecular adsorption of ethanol occurred on oxidized Al films. Adsorption of ethanol on Ni and Al films gave rise to metal oxidation through the reaction of surface ethoxides by which gaseous ethane and hydrogen were formed. Dehydrogenation of ethanol occurred mainly on Pd films and the formation of acetaldehyde, together with carbon monoxide and some methane, was observed. Dehydration of ethanol proceeded on oxidized Ni film resulting in the liberation of ethylene gas. The production of CO_2 gas subsequent to ethanol adsorption on oxidized Ni and Pd films occurred, probably through the formation of acetate radicals on the surface. Parallel experiments using monodeuterated ethanol were carried out on all surfaces with the aim of understanding the modes of alcohol adsorption and decomposition on metal surfaces. The rate of ethanol adsorption on each surface depended directly on the ethanol pressure to the first power and the activation energy (E_a) of adsorption was not a function of the extent of adsorption. A linear relationship was found between E_a and the logarithm of the pre-exponential factor of the rate equation, suggesting the operation of a compensation effect in the alcohol adsorption and decomposition on the films. Ethanol was found to have a greater tendency for adsorption and decomposition on the metals than methanol. A sequence was suggested for the activity of the various surfaces in alcohol adsorption and decomposition.

There have been quite a number of investigations of ethanol with bulk metals, bulk oxides, reduced powders as well as on many commercial catalysts.[1-6] Little direct information is available concerning the chemisorption and the decomposition of ethanol on evaporated metal films.[7] There is, therefore, a need for a fundamental investigation of ethanol adsorption on clean metal films under controlled conditions of temperature and pressure.

We have selected nickel, palladium and aluminium on which the adsorption and decomposition studies have been performed. The effect of oxygen was also studied by following the adsorption of ethanol on films which had been saturated with oxygen. Adsorption of monodeuterated ethanol on the same films was investigated with the aim of understanding the reactivity of the oxygen–hydrogen bond as well as the modes of adsorption and decomposition on the surface.

EXPERIMENTAL

The preparation of the metal films was as described in Part 1 (previous paper).

Ethanol was a spectroscopic sample obtained from Hopkin and Williams and was thoroughly degassed by repeated freezing and pumping operations. Oxygen was prepared by heating AnalaR $KMnO_4$ after thorough degassing. Krypton was obtained from the British Oxygen Co. in sealed glass bulbs. Both oxygen and krypton were further purified before use. The gas phase was analysed using a Quadruvac 200 mass-spectrometer partial-pressure gauge, obtained from

Lybold-Heraus, which operated on the quadrupole principle and covered the mass range 1-200 a.m.u. The instrument was combined with a pressure converter which could reduce the gas pressure under analysis to $< 10^{-1}$ N m^{-2} without influencing its composition. The gauge head of the mass spectrometer for ion detection was supplemented by a Faraday cup for partial analysis down to 10^{-6} N m^{-2}.

RESULTS

EXTENT OF ADSORPTION

The extent of ethanol adsorption on a clean film at any stage may be expressed as

$$\theta = V_e / V_{Kr}$$

where V_e represents the volume of ethanol adsorbed and V_{Kr} the volume of the krypton monolayer on the film, obtained from the krypton adsorption isotherm at 78 K. Ethanol in the pressure range 1-14 N m^{-2} was admitted to the film at 223 K, and its interaction with the film was followed until the rate of uptake fell below 10^{-4} mm^3 s^{-1} cm^{-2}. The film was then warmed in successive stages to 450 K.

TABLE 1.—ADSORPTION OF ETHANOL ON FILMS OF Ni, Pd AND Al AT 223 K

film	$V_{Kr}{}^a$	$V_e{}^a$	θ
Ni	17	19.6	1.15
Pd	67	107.0	1.60
Al	6.2	10.8	1.75

[a] Volumes are expressed in mm^3 at s.t.p.

ETHANOL ON NICKEL

The initial doses of ethanol ($\theta < 0.7$) were instantaneously adsorbed on the Ni film at 223 K to a final pressure of 10^{-3} N m^{-2}; further adsorption proceeded at a rate which decreased as θ increased; such adsorption was accompanied by the slow liberation of hydrogen. The rate of ethanol adsorption became $< 10^{-4}$ mm^3 s^{-1} cm^{-2} when θ was 1.1; the results of adsorption on Ni films at 223 K are given in table 1.

On rapid warming of the Ni film to 290 K further ethanol adsorption took place and the pressure of the liberating hydrogen increased by some 20%. The rate of ethanol uptake increased at 313 K and the gaseous products consisted of H_2, C_2H_6, CH_3CHO and, to a lesser extent, CH_4 and CO. As the temperature of the Ni film increased (> 313 K) further enhancement in the rate of ethanol uptake was observed and the pressures of the gaseous products, with the exception of CH_3CHO, increased considerably. The pressure of CH_3CHO decreased with time at 373 K and there was no further liberation of acetaldehyde at temperatures up to 450 K. A typical plot representing the liberation of the gaseous products through the interaction of ethanol with Ni film is shown in fig. 1. The rate of ethanol adsorption and those for the liberation of the decomposition products became immeasurably fast at temperatures > 450 K. The rate of adsorption at a given temperature was the same in the presence or the absence of the reaction products.

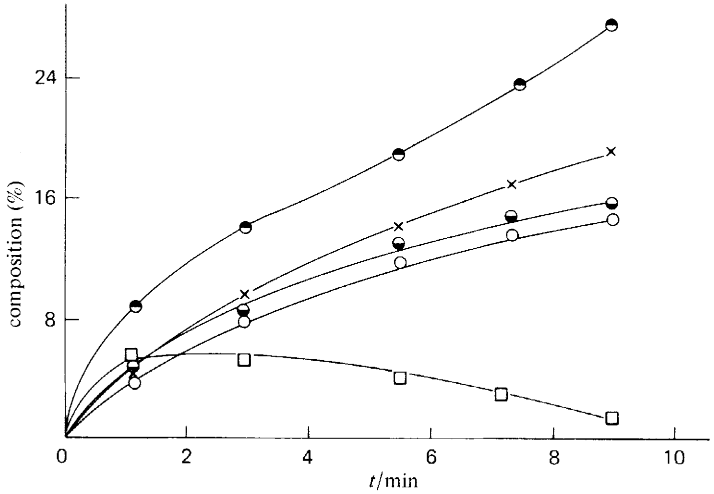


FIG. 1—Analysis of the gas phase throughout ethanol interaction with Ni film at 373 K. The points on each plot represent changes in the percentage (%) of the gas with time. ◓, ethane; ×, CO; ◒, H_2; ○, CH_4; □, CH_3CHO. The points corresponding to ethanol were deleted.

ETHANOL ON PALLADIUM

Palladium films behaved toward ethanol at 223 K generally in the same way as did Ni films. The slow ethanol adsorption, subsequent to the initial fast uptake, on Pd film began at $\theta = 0.95$ and was accompanied by the evolution of some acetaldehyde. The rate of adsorption became 10^{-4} mm^3 s^{-1} cm^{-2} at $\theta = 1.6$. The results of adsorption for a typical experiment at 223 K are shown in table 1.

When the Pd film was warmed to 290 K, further ethanol adsorption occurred, which was accompanied by CH_3CHO evolution. The rate of ethanol adsorption on Pd at 333 K was greater and gases such as CH_3CHO, CO, H_2 and CH_4 were formed. The pressure of CH_3CHO decreased with time at temperatures > 333 K, while there was a considerable increase in the amounts of the other gaseous products as more ethanol were taken up. Some ethane was also detected in the gas phase at temperatures $\geqslant$ 363 K. Fig. 2 shows the analysis of the gas phase with time throughout the ethanol adsorption on the film at 393 K.

ETHANOL ON ALUMINIUM

Fast irreversible adsorption of ethanol took place on Al film at 223 K to a final pressure of 10^{-3} N m^{-2} at $\theta < 1.3$. Further slow ethanol adsorption, accompanied by H_2 and C_2H_6 evolution, continued until $\theta = 1.6$ at which the rate of ethanol uptake became extremely slow (table 1). Further ethanol adsorption was possible at $\geqslant$ 290 K and the rate increased with temperature. At 323 K, the adsorption of ethanol caused a subsequent evolution of H_2, C_2H_6, CO and CH_4. The evolution of ethane was more pronounced when ethanol was adsorbed on Al film at $\geqslant$ 353 K. No acetaldehyde was detected in the gas phase at any stage throughout the ethanol adsorption on Al film in the temperature range 223-450 K (fig. 3).

ADSORPTION OF ETHANOL ON OXIDIZED FILMS

In these experiments the film was first saturated at 290 K and oxygen pressure of 4 N m^{-2} with pure oxygen, the excess gaseous oxygen was then pumped out and ethanol was admitted to the film at 223 K in doses each of *ca.* 5-8 N m^{-2} and the adsorption was followed as with the clean films. The data obtained for the oxygen uptake, the subsequent ethanol adsorption and the corresponding values of Y are given in table 2, where Y is defined as

$$Y = V_e/\bar{V}_{Kr}$$

where V_e represents the volume of ethanol uptake and $\bar{V}_{Kr}$ the volume of the krypton monolayer on the oxidized film.

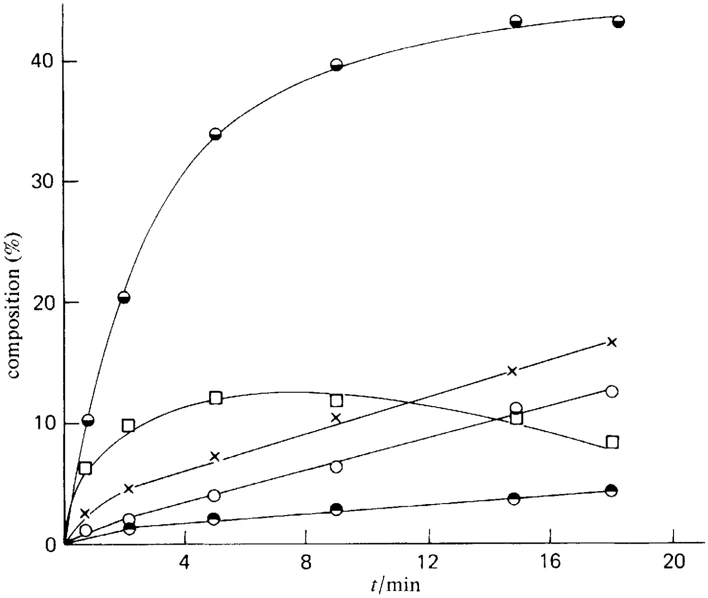


FIG. 2.—Analysis of the gas phase for the interaction of ethanol with a Pd film at 393 K. The symbols are as in fig. 1.

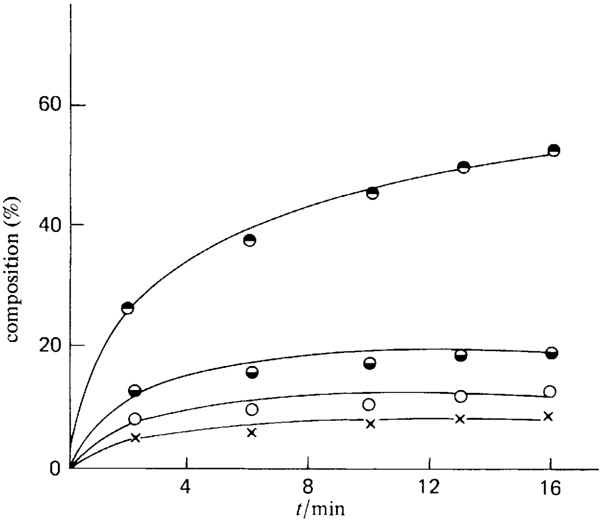


FIG. 3.—Gas-phase analysis throughout the adsorption of ethanol on Al film at 373 K.

At 223 K there was a fast adsorption of ethanol which was, thereafter, followed by a slow uptake until Y was 2.14 on Ni and 1.95 on Pd; *ca.* 5% of the adsorption on Ni and 20% of the uptake on Pd were reversible. Adsorption of ethanol on both films at this temperature was not accompanied by the liberation of gases.

Further ethanol adsorption occurred on Ni and Pd films, at temperatures $\geqslant 290$ K and its rate increased with temperature. The major gaseous products at such temperatures were C_2H_4, H_2O, C_2H_6, CO_2, CH_4 and H_2 on Ni and CH_3CHO, H_2O, CH_4, CO_2, CO, H_2 and C_2H_6 on Pd.

Table 2.—Adsorption of ethanol on oxidized films of Ni, Pd and Al at 223 K[a]

film	V_{Kr}	V_{O_2}	$\bar{V}_{Kr}$	V_e	Y
Ni	19.2	73.4	15	32	2.14
Pd	37.0	117.0	32	62.4	1.95
Al	4.5	6.1	7.1	8.5	1.20

[a] Volumes are expressed in mm^3 at s.t.p.

Fast adsorption of ethanol occurred at 223 K on Al films which had adsorbed oxygen until $Y = 0.7$. Beyond such a coverage the adsorption was slow and the film became saturated with ethanol at $Y = 1.2$. Some 20% of the adsorbed ethanol was desorbed on warming the films to 290 K. When the film was heated in successive stages in the presence of ethanol to 423 K desorption took place; the value of Y decreased to 0.65 at 333 K and to 0.32 at 400 K. A small quantity of diethyl ether, amounting to *ca.* 5% of the adsorbed ethanol at 400 K, was detected with the desorbed ethanol at this temperature.

ADSORPTION OF C_2H_5OD

The adsorption of monodeuterated ethanol C_2H_5OD was studied on the clean and the oxidized metal films in an exactly similar way to that of C_2H_5OH. The gas phase at temperatures > 223 K contained such products as D_2, HD, CO, H_2, CH_4, CH_3D, C_2H_6 and C_2H_5D. Table 3 shows the composition of the gas phase at three temperatures in terms of the percentage of each gas in the mixture. On oxidized films of Ni and Pd, the adsorption and the decomposition of C_2H_5OD took place exactly

Table 3.—Gas-phase analysis for the adsorption and decomposition of [$^2H_1$]ethanol at three successive temperatures

film	temp/K	CH_3CHO	D_2	HD	H_2	CO	CH_4	CH_3D	C_2H_6	C_2H_5D
Ni	333	11.3	3.0	7.9	4.0	6.0	3.0	5.0	9.0	11.0
	363	3.8	3.0	8.0	3.0	12.0	4.0	7.1	7.0	28.0
	393	3.0	2.5	7.0	3.0	13.0	3.5	6.0	10.0	43.0
Pd	333	19.4	3.0	9.5	2.0	7.0	—	2.0	0.2	—
	363	6.0	5.0	13.0	8.0	16.0	4.0	6.0	2.0	3.0
	393	2.8	9.0	20.0	11.0	25.0	10.0	11.5	3.5	5.0
Al	333	—	5.0	6.1	1.6	9.4	3.5	5.0	4.8	29.0
	393	—	5.8	8.3	2.9	11.1	4.6	6.2	5.8	33.0
	423	—	3.5	11.0	4.0	13.0	6.0	8.0	7.5	44.0

TABLE 4.—ANALYSIS OF THE GAS PHASE THROUGHOUT THE INTERACTION OF C_5H_5OD WITH OXIDIZED Ni AND Pd FILMS AT 423 K

	percentage in the gas phase	
products	oxid. Ni	oxid. Pd
C_2H_4	37	—
HDO	15	12.4
D_2O	10	7.0
C_2H_5D	7	—
C_2H_6	4	6.0
CO_2	4	15.0
CO	4	7.0
CH_3D	7	14.1
CH_4	3	6.0
H_2O	3	2.0
HD	1.5	3.5
H_2	1.5	1.5
D_2	0.3	4.0
CH_3CHO	—	22.0

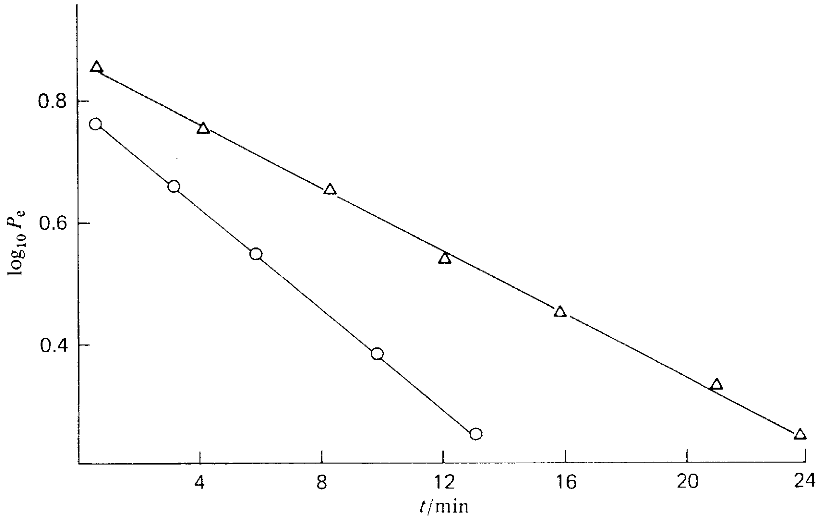


FIG. 4.—First-order plots for the adsorption of ethanol on Ni (○) at 333 K and Al (△) at 393 K. The ethanol pressure (P_e) was expressed in N m^{-2}.

as with C_2H_5OH. The desorption of the decomposition products became considerable at temperatures ⩾ 290 K. Table 4 shows the analysis of the gas phase throughout the interaction of C_2H_5OD with oxidized Ni and Pd films at 423 K.

KINETICS OF ETHANOL ADSORPTION

The dependence of the reaction rate on ethanol pressure was found from a great number of measurements[8, 11] to be unity. A check of this result was to plot log P_e

against time for various films as shown in fig. 4. The activation energy (E_a) of ethanol adsorption and the pre-exponential factor (A) of the rate equation did not alter with the variation of θ or Y. The values of E_a and A for different films were derived from Arrhenius plots, a typical example of which is shown in fig. 5. Table 5 gives the values of E_a and A for the different surfaces over the temperatures range 290-4300 K. A linear relationship was found to exist between the values of log A and those of E_a, with the exception of Al, as shown in fig. 6.

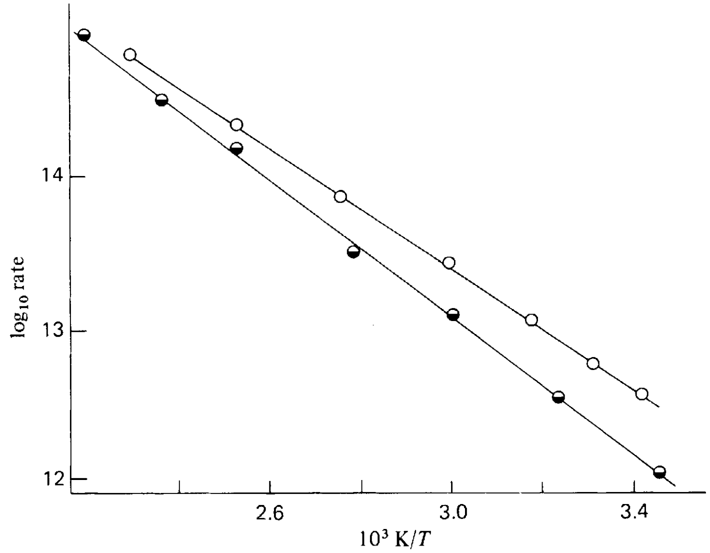
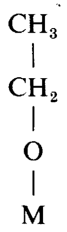


FIG. 5.—Arrhenius plots for the interaction of ethanol with Ni (○) and oxidized Ni (◒) films. The rate of ethanol adsorption was expressed in molecule cm^{-2} s^{-1}.

DISCUSSION

ADSORPTION AT 223 K

The evolution of H_2 from Ni, $H_2+C_2H_6$ from Al and of H_2+CH_3CHO from Pd films subsequent to ethanol adsorption at 223 K suggests that the adsorption on these metals at such temperatures was to some extent dissociative. The adsorbed phase at 223 K may involve ethoxide radicals CH_3CH_2O(a), acetaldehyde(a) and hydrogen H(a), together with some molecularly adsorbed ethanol CH_3CH_2OH(a), where (a) denotes an adsorbed species. The ethoxide radicals were probably the most abundant species on the surface, bonding to the surface atoms (M) in the following manner:[4, 5, 12]


$$\begin{array}{c} CH_3 \\ | \\ CH_2 \\ | \\ O \\ | \\ M \end{array}$$

Adsorption of ethanol on clean films of Ni and Pd, which had been saturated with oxygen at 290 K, occurred to a greater extent than on the clean films; the values of

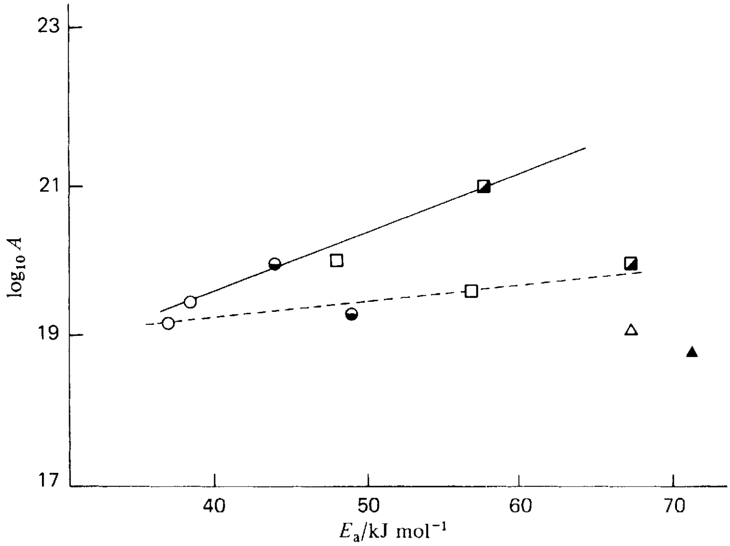


FIG. 6.—Variation of log A with E_a for the interaction of ethanol with Ni (○), Pd (□), Al (△), oxidized Ni (◒) and oxidized Pd (◪). The dotted line represents the corresponding relationship for the methanol interaction with the same surfaces. (▲) was used for Al in the case of methanol. A was expressed in molecule cm^{-2} s^{-1}.

Y in table 2 were shown to be appreciably greater than the corresponding values of θ in table 1. This may be attributed to some weak molecular adsorption on the chemisorbed layer which could be removed merely by warming the films to 290 K. The extent of ethanol adsorption on the oxidized Al film (table 2) was less than on the clean metal surface (table 1) and a substantial fraction of the adsorption was molecular which could be removed from the film on heating to 400 K.

ADSORPTION BETWEEN 290 AND 400 K

The types and the extents of the gaseous products due to ethanol adsorption on Ni, Pd and Al films increased as the temperature of the film increased above 290 K. The formation of the gaseous products may take place through the surface ethoxide undergoing two main types of decomposition: (i) by the cleavage of the carbon–oxygen bond to form ethyl radicals and oxygen atoms on the surface; the latter is utilized in the subsequent metal oxidation. The resulting ethyl radicals may combine with the adsorbed hydrogen atoms to form ethane which enters the gas phase. These reactions may be represented as

$$CH_3CH_2OH(g) \rightarrow CH_3CH_2O(a) + H(a) \quad (1\,a)$$

$$CH_3CH_2O(a) \rightarrow CH_3CH_2(a) + O(a) \quad (1\,b)$$

$$CH_3CH_2(a) + H(a) \rightarrow C_2H_6(g) \quad (1\,c)$$

also

$$H(a) + H(a) \rightarrow H_2(g). \quad (1\,d)$$

(ii) The surface ethoxide may be converted into adsorbed acetaldehyde which may then undergo a series of reactions on the surface resulting in the formation of other products as

$$CH_3CH_2O(a) \rightarrow CH_3CHO(a)+H(a) \qquad (2a)$$

$$CH_3CHO(a) \rightarrow CH_3CO(a)+H(a) \qquad (2b)$$

$$CH_3CO(a) \rightarrow CH_3(a)+CO(g). \qquad (2c)$$

It has been found[13] that CH_3CO radicals decompose readily even in the absence of a metal surface at temperatures not exceeding 570 K to give methyl radicals and carbon monoxide in accordance with reaction (2*c*). The C—C bond dissociation energy in CH_3CO is known[14] to be *ca.* 46.2 kJ mol^{-1} while it is 315 kJ mol^{-1} in CH_3CHO, suggesting the favouring of reaction (2*c*) over that involving the direct rupture of $CH_3CHO(a)$ into $CH_3(a)$ and $CHO(a)$ species. This assumption does not consider the heats of adsorption for the various species resulting from the dissociations. The adsorbed methyl radicals may interact with hydrogen adatoms to form methane as

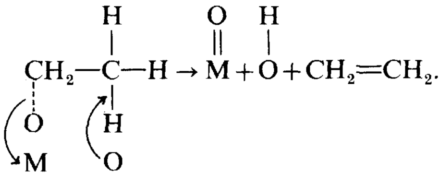
$$CH_3(a)+H(a) \rightarrow CH_4(g). \qquad (2d)$$

TABLE 5.—ACTIVATION ENERGIES (E_a) AND THE PRE-EXPONENTIAL FACTORS (A) FOR THE INTERACTION OF ETHANOL WITH Ni, Pd AND Al FILMS

film	E_a/kJ mol^{-1}	A/molecule s^{-1} cm^{-2}
Ni	38.4	2.7×10^{19}
Pd	48.0	6.0×10^{19}
Al	67.5	1.26×10^{19}
oxid. Ni	44.0	9.55×10^{19}
oxid. Pd	57.7	1.0×10^{21}

Reactions such as (1*a*)-(1*d*) predominate on Ni and Al films due possibly to the large tendency of both metals for oxygen uptake.[9,10]

The main gaseous products on oxidized Ni films involved ethylene and water vapour at temperatures > 333 K. Thus oxidized nickel acting as a dehydrating catalyst for the ethanol according to such reactions as:



$$\underset{\underset{M}{\overset{\vdots}{O}}}{CH_2}-\overset{H}{\overset{|}{\underset{\underset{O}{H}}{C}}}-H \rightarrow \overset{O}{\overset{\|}{M}}+\overset{H}{\overset{|}{O}}+CH_2{=}CH_2. \qquad (3a)$$

The dehydration probably occurs through a typical acid–base catalysed mechanism[12] in which the metal cation acts as a weak acid interacting with the ethoxide oxygen as a base; the interaction is accompanied by the simultaneous breakage of the carbon–oxygen and carbon–hydrogen bonds of ethanol. Reaction (3*a*) may be followed by

$$OH(a)+H(a) \rightarrow H_2O(g). \qquad (3b)$$

The formation of CO_2 gas may take place through the reaction of the surface ethoxide to form $CH_3CHO(a)$ and $CH_3CO(a)$ according to reactions (2*a*) and (2*b*) followed by surface oxidation of $CH_3CO(a)$ to acetate radicals in a similar manner to the formation of formate throughout the decomposition of methanol on the oxidized films[15]

$$CH_3CO(a) + O(a) \rightarrow CH_3COO(a). \tag{4a}$$

The C—C bond of the acetate may then rupture as:

$$CH_3COO(a) \rightarrow CH_3(a) + CO_2(g). \tag{4b}$$

The methyl radicals may combine with H(a) to form $CH_4(g)$ as in reaction (2*d*).

No ethylene was formed on oxidized Pd subsequent to the adsorption of ethanol at temperatures > 290 K. The main reaction on the oxidized Pd above 290 K involved the dehydrogenation of the alcohol to produce gaseous acetaldehyde. It has been suggested[12] that such changeover from a dehydration to a dehydrogenation behaviour requires a metal catalyst with a lower electronegativity; Pd has a lower electronegativity (1.35) than nickel (1.75).

ADSORPTION OF CH_3CH_2OD

The adsorption and decomposition of monodeuterated ethanol on metal films of Ni, Pd and Al, as well as on their oxidized surfaces, proceeded in a similar manner to the adsorption of ethanol on the same surfaces under similar experimental conditions. The liberated hydrogen involved H_2, HD and D_2 gases; the formation of such gases is expected due to the presence of D(a) *via* reaction (1*a*) and of H(a) by such reactions as (2*a*) and (2*b*). The production of CH_3D may indicate the existence of methyl radicals on the surface due to the rupture of the C—C bond of ethanol by such reaction as (2*c*). The liberation of ethane C_2H_6 and of monodeuterated ethane C_2H_5D on the clean films may occur as a consequence of the reaction of the ethyl radicals [reaction (1*b*)] with adsorbed hydrogen [reactions (2*a*)-(2*b*)] and deuterium adatoms resulting in a reaction similar to reaction (1*a*). It may also be reasonable to suggest that the formation of C_2H_5D on oxidized Ni occurs through the hydrogenation of ethylene by gaseous HD. The fact that supports this latter suggestion is that no gaseous C_2H_5D was detected on oxidized Pd films (table 4), which showed no tendency for ethylene formation.

In general, the types and quantities of the gaseous products formed subsequent to CH_3CH_2OD adsorption on the metal films support the proposed mechanisms for ethanol decomposition on the surfaces. There are a few other facts that merit some remarks. (1) No deuterated acetaldehyde or ethylene was ever detected in the gas phase as a consequence of ethanol decomposition on the films. (2) No multiple exchange was observed at any stage with methane or ethane liberated in the course of ethanol adsorption, and decomposition of gaseous methane on the films was as CH_4 and CH_3D and that of ethane was as C_2H_6 and C_2H_5D.

These facts indicate that the mechanism of the multiple exchange by repeated second-point adsorption does not operate throughout the adsorption of ethanol on Ni, Pd and Al films. Anderson and Kemball[7] have shown that the distribution of the initial products in the exchange of ethanol with deuterium on rhodium, iron and palladium metals at temperatures ranging from 273 to 373 K involved mainly CH_3CH_2OD; its percentage in the [$^2H_1$] to [$^2H_6$]deuterated ethanols ranged from 85 to 100%.

KINETICS OF ADSORPTION

The pressure dependence of ethanol adsorption on the metal films, together with the constancy of the activation energy of adsorption on each metal regardless of the extent of adsorption (θ or Y), suggest that the rate-determining step probably involves the adsorption of ethanol followed by its decomposition into ethoxide radicals and hydrogen atoms on the surface. The relationship observed between log A and E_a (fig. 6) suggests the operation of a compensation effect[16, 17] in the kinetics of ethanol adsorption on the clean and oxidized films of Ni and Pd. A similar relationship for the adsorption of methanol on the same surfaces[18] is also shown in fig. 6. The lines for both methanol and ethanol adsorption approach each other at low values of E_a and A; the methanol line is shown to be more horizontal than that of ethanol. The higher gradient of the log A against E_a plot in the case of ethanol reflects a greater compensation effect. Comparing the kinetic behaviour of the two alcohols it may be possible to make the following deductions. (1) The adsorption of ethanol is in general less dependent on the activation energy but more dependent on the pre-exponential factor, than is the case for methanol. (2) The points corresponding to Al for both alcohols shifted considerably from the linear relationship of fig. 6. This may be due to the formation of an adherent and self-healing oxide[19] film on the metal surface subsequent to reaction (1*b*), thus decreasing the contribution of the metal sites to further adsorption and decomposition of the alcohol with a consequent increase in E_a. (3) The relative stability of the ethoxides was generally less than that of the methoxides. Bradley[20] has reported that the stabilities of the zirconium alkoxide followed the sequence:

$$\mathrm{Zr(OCH_3)_4 > Zr(OCH_2CH_3)_4 > Zr[OCH(CH_3)_2]_4}.$$

The stability of surface alkoxides can hardly be correlated with[21] the strength of the α-hydrogen of the C—H bond in ethanol (370 kJ mol^{-1}) and in methanol (386 kJ mol^{-1}). Furthermore, the energy involved in the disruption of the RO—H bond is known[22] to be the same for both alcohols; the rates of the formation of the alkoxides should therefore be approximately the same. The difference in the rate and the tendency for the decomposition of the two alcohols may then be ascribed to the stability of the alkoxide intermediates on the surface. Oxidation of methanol and ethanol to their corresponding aldehydes was examined over an iron–molybdenum catalyst[23] in the temperature range 453-513 K, and the reactivity of ethanol was found to be higher than that of methanol. The oxidations of methanol and ethanol were similarly compared over thorium molybdate catalyst[24] in the temperature range 493-553 K, and ethanol was again found to oxidize more readily than methanol: the activation energies for oxidation of ethanol were *ca.* 12.6-25.2 kJ mol^{-1} lower than the corresponding values for methanol oxidation.

The relatively higher values of A, combined with lower E_a, in the case of ethanol adsorption (fig. 6) on all surfaces should result in a greater reaction rate than that of methanol. The only exception to this conclusion is the behaviour of the clean Ni in fig. 6, which is shown to be almost the same for both alcohols. This may be due to the fact that metal oxidation was the main feature of the interaction for both alcohols on this metal and the behaviour probably reflects the high tendency of Ni for oxygen attraction and extraction from both alcohols. This argument may apply to some extent to the behaviour of Al towards both methanol and ethanol, and the points corresponding to the two alcohols in fig. 6 are also close to each other.

A further point which merits some attention is that the sequence in the variation of E_a and log A values for both alcohols was the same:

$$\text{Ni} < \text{oxidized Ni} < \text{Pd} < \text{oxidized Pd} < \text{Al}.$$

Aluminium was inserted in the sequence merely on the basis of its E_a value. Thus the activity of the different surfaces for alcohol adsorption and decomposition could be arranged as:

$$\text{Ni} > \text{oxidized Ni} > \text{Pd} > \text{oxidized Pd} > \text{Al}.$$

There are very few kinetic data in the literature for the adsorption of alcohols on metals and metal oxides. Activation energies for the hydrogenation of several alcohols over alumina-supported metals have been reported.[25] With the primary alcohols the activation energy shown by each metal decreases with increasing molecular weight. The sequence of activation energies was the same for each alcohol on different alumina-supported metals. An activation energy of 63 kJ mol^{-1} was given for the dehydrogenation of ethanol over an alumina-supported nickel catalyst.

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