63. *The Desorption of Alcohols from Metal Oxides. Part I. Ethanol and Propan-2-ol.*

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Ethanol and propan-2-ol were adsorbed on cupric, nickel, zinc, aluminium, and titanium oxides at room temperature. In each case, the products desorbed over a series of ranges of temperature were collected and analysed by gas chromatography. The extent and the nature of the decomposition vary widely from one oxide to another. Similar types of product are formed from both alcohols desorbed from a given oxide, although propan-2-ol is always the more readily decomposed.

Some combustion of the alcohols together with partial reduction of the oxides occurs over cupric and nickel oxides. Thermodynamic calculations confirm that such combustion is feasible. Products containing one more carbon atom than the adsorbed alcohol are formed over nickel oxide and zinc oxide.

Catalytic decomposition of alcohols over metal oxides at high temperatures has been the subject of considerable investigation, and the adsorption of alcohols on oxides at lower temperatures has also been studied. However, little information is available about the nature of the products which are formed when alcohols are desorbed from oxides at temperatures intermediate between room temperature and the temperature required for genuine catalytic decomposition of the alcohol. Schreiner and Kemball [1] reported that considerable decomposition of ethanol occurred when attempts were made to desorb it from a number of metal oxides. In view of the variety of products which Schreiner [2] observed, a detailed study has been made of the desorption products from a series of alcohols over a number of oxides. Schreiner's observations were mainly qualitative as the products were too numerous to be analysed efficiently by the mass-spectrometric technique which he used. Gas chromatography now provides a means of accurate and rapid analysis. This paper describes results obtained for the desorption of ethanol and propan-2-ol from a number of oxides, and also one set of observations on the desorption of acetaldehyde from zinc oxide. Results for higher alcohols will be given in Part II.

EXPERIMENTAL

" AnalaR " ethanol and propan-2-ol, and a B.D.H. sample (99% pure) of acetaldehyde were used. Nickel oxide was prepared by heating nickel carbonate (B.D.H.) at 860° for 2 days and the product was washed with dilute hydrochloric acid and then distilled water. The titania samples " Anatase HR " and " Rutile 272 " were supplied by British Titan Products. " AnalaR " oxides of zinc, copper, and aluminium were used and a second sample of alumina, η-Al_2O_3, prepared from the alcoholate was supplied by Imperial Chemical Industries Limited, Billingham.

The apparatus consisted of a conventional high-vacuum train with provision for measuring the adsorption of alcohol by means of a mercury manometer and for the collection, estimation, and handling of the desorption products. After a weighed sample of the oxide had been heated *in vacuo* at a temperature consistent with its stability (CuO at 200°; other oxides at 400°), the oxide was cooled, sufficient alcohol vapour was admitted to saturate the surface at room temperature, and the amount adsorbed was determined. Desorption was then started at room temperature, to a trap cooled in liquid nitrogen. Any non-condensable products were removed by a Toepler pump. After 20—30 hr., when the rate of desorption of products had fallen below about 0·1 ml. (N.T.P.)/hr., the products were removed for analysis. The temperature of the oxide was raised by about 50° and a second range of desorption products collected in a similar manner. This procedure was repeated up to a final temperature identical with that used for

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[1] Schreiner and Kemball, *Trans. Faraday Soc.*, 1953, **49**, 292.
[2] Schreiner, Ph.D. Thesis, Cambridge, 1951.

outgassing the oxide. The total amounts of both condensable and non-condensable products collected at each temperature were measured and samples of each were analysed by gas chromatography.

The detectors in the gas-chromatographic units were thermal-conductivity cells containing 48 S.W.G. platinum wire. These were heated by either alternating or direct current. The off-balance potential was either amplified and recorded on an Evershed and Vignoles A.C. milliammeter or recorded directly on a Sunvic D.C. millivoltmeter. Several types of column were used in the analyses. A 6 ft. charcoal (44—60 mesh B.S.S.) column gave good resolution of the non-condensable gases, hydrogen, carbon monoxide, and methane. An 8 in. charcoal column was used for separating carbon dioxide, ethylene, and ethane. The conditions of operation and the performance of both these columns have been described by Darby and Kemball.[3] Greater accuracy in the estimation of carbon dioxide and ethylene was obtained later by using a 16 in. charcoal column at 63° with hydrogen as carrier at a flow rate of 168 ml./min. Columns containing commercial dinonyl phthalate (D.N.P.) on Celite (1 : 2·2 by wt.) were used for analysing all other products. The operating conditions and the sensitivities for the various substances resolved on the phthalate–Celite columns are shown in Table 1. Column A was only used in the early stages of the work because more accurate results were obtained by using column C with hydrogen as carrier gas. Peak heights were used for estimating compounds which gave sharp peaks, and peak areas were used for estimating compounds giving more diffuse peaks.

TABLE 1. *Calibrations for dinonyl phthalate–Celite columns.**

Column	Operating conditions	Substance	Elution time (min.)	Response (μv/mm.)	Limit of detection (mm.)
A	N_2; 35 ml./min.	H_2O	5·50	7·4	1·61
	35°; 6 ft.	$C_2H_5{\cdot}OH$	11·50	17·1	0·63
	ΔP = 280 mm.				
	S = 5 ml.				
B	H_2; 118 ml./min.	H_2O	2·70	3·7	0·68
	40°; 6 ft.	$(CH_3)_2CO$	3·01	26·5	0·09
	ΔP = 670 mm.	$(iso\text{-}C_3H_7)_2O$	5·10	10·0	0·25
	S = 5 ml.	$iso\text{-}C_3H_7{\cdot}OH$	5·67	11·5	0·22
C	H_2; 85 ml./min.	$CH_3{\cdot}CHO$	1·27	54·1	0·05
	33°; 4 ft.	$(C_2H_5)_2O$	2·07	38·8	0·06
	ΔP = 692 mm.	H_2O	2·4—2·6	2·9	0·86
	S = 5 ml.	$C_2H_5{\cdot}OH$	3·40	16·9	0·14
		$(CH_3)_2CO$	3·60	17·9	0·14
		$(iso\text{-}C_3H_7)_2O$	4·5	20·2	0·12
		$iso\text{-}C_3H_7{\cdot}OH$	4·9	16·1	0·15
D	H_2; 57 ml./min.	C_2H_4, C_2H_6	2·6	176	0·014
	20°; 30 ft.	C_3H_6, C_3H_8	3·3—3·4	111	0·022
	ΔP = 684 mm.	$iso\text{-}C_4H_{10}$	4·8	90	0·03
	S = 14 ml.	$n\text{-}C_4H_{10}$	6·4	95	0·03
		$1\text{-}C_4H_8$	7·9	90	0·03
		$2\text{-}C_4H_8$	8·8	90	0·03

* The operating conditions given include carrier gas, flow rate, temperature, and length of column, pressure difference across column, and size of sample admitted. In each case, gas entered the columns at atmospheric pressure.

A small peak corresponding to water was always found when samples of ethanol were passed through the chromatographic units even when the alcohol had been treated with anhydrous potassium carbonate. It was thought that these peaks resulted from water displaced from the glass walls of the apparatus by the vapour of alcohol. Corrections were made to allow for this when analysing samples. No peaks corresponding to water were observed when propan-2-ol or acetaldehyde was passed through the columns.

RESULTS

Approximate surface areas for each oxide were calculated by assuming that the cross-sectional area for both alcohol molecules is 20 Å ^{2} and that the amount adsorbed at room temperature corresponded to coverage of the surface by a monolayer. The surface areas are shown in

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[3] Darby and Kemball, *Trans. Faraday Soc.*, 1957, **53**, 832.

TABLE 2. *Approximate surface areas of the oxides* (*m*^{2}./*g*.).

Adsorbate	ZnO	CuO	NiO	α-Al_2O_3	TiO_2 (anatase)	TiO_2 (rutile)
C_2H_5·OH	4·1	9·9	0·6	0·7	6·6	4·4
iso-C_3H_7·OH	3·9	11·3	0·5	0·4	5·0	3·5

TABLE 3. *Recovery of ethanol from the oxides.*

	Alcohol recovered		Lowest	Temp. to which	Total recovery (%)		
Oxide	at room temp. (%)	total (%)	temp. for decomp.	alcohol persists	C	H	O
CuO	44·6	48·8	17°	128°	90	106	393
NiO	43·9	82·0	19	216	105	103	157
ZnO	16·2	26·5	42	102	125	122	91
α-Al_2O_3 ...	46·6	80·0	65	300	100	98	121
η-Al_2O_3 ...	19·2	51·8	48	205	100	100	100
Anatase ...	42·9	95·0	103	300	100	99	104
Rutile	58·1	95·0	98	305	99	98	101

TABLE 4. *Recovery of propan-2-ol from the oxides.*

	Alcohol recovered		Lowest	Temp. to which	Total recovery (%)		
Oxide	at room temp. (%)	total (%)	temp. for decomp.	alcohol persists	C	H	O
CuO	49·8	54·3	19°	95°	99	102	257
NiO	52·7	66·9	23	169	100	99	161
ZnO	3·2	4·5	21	92	92	90	87
α-Al_2O_3 ...	25·4	70·5	20	220	86	90	111
Anatase ...	38·7	89·7	51	198	101	101	113
Rutile	57·1	92·7	52	148	99	98	107

TABLE 5. *Decomposition products formed from adsorbed ethanol* (*molecules*/100 *molecules of ethanol adsorbed*).

Oxide	H_2O	C_2H_4	$(C_2H_5)_2O$	H_2	CH_3·CHO	CH_4	CO	CO_2	C_3	C_4
CuO	168	—	—	—	—	—	—	90·6	—	1·0
NiO	35·4	—	—	—	—	—	—	19·8	9·1	—
ZnO	7·6	52·2	—	101	—	13·0	12·1	22·5	11·7	3·0
α-Al_2O_3 ...	9·5	—	—	17·5	—	1·5	—	15·6	5·9 [a]	
η-Al_2O_3 ...	40·2	32·5	7·8	0·4	—	0·02	—	0·1	—	—
Anatase...	2·4	0·7	—	0·2	3·1	—	—	1·7	—	0·1
Rutile ...	1·5	—	—	0·3	1·4	—	—	1·4	—	0·6

[a] Mixture of C_3 to C_5 hydrocarbons

TABLE 6. *Decomposition products formed from adsorbed propan-2-ol* (*molecules*/100 *molecules of propan-2-ol adsorbed*).

Oxide	H_2O	C_3H_6	$(iso\text{-}C_3H_7)_2O$	H_2	$(CH_3)_2CO$	CH_4	CO_2	C_2	C_4
CuO	95·1	—	—	—	31·8	—	37·8	—	—
NiO	43·6	4·4	4·8	—	6·5	—	19·9	—	4·3
ZnO	26·0	28·0	5·4	62·8	1·3	6·4	25·0	—	27·9
α-Al_2O_3 ...	27·7	1·9	—	5·6	10·0	—	5·3	2·8	—
Anatase ...	12·1	1·5	—	—	9·3	—	1·1	—	—
Rutile	3·6	—	—	2·8	4·8	—	3·1	—	—

TABLE 7. *The desorption of ethanol from zinc oxide* (*molecules*/100 *molecules of ethanol adsorbed*).

Temp. range	C_2H_5·OH	H_2O	C_2H_4	H_2	CH_4	CO	CO_2	C_3	C_4
17°	16·20	—	—	—	—	—	—	—	—
17—42	6·66	—	—	—	—	—	—	—	—
42—67	3·46	—	0·98	—	—	—	—	—	—
67—102	0·18	0·29	5·28	17·29	—	—	—	—	—
102—148	—	1·20	39·87	47·30	—	—	—	—	—
148—198	—	0·62	6·04	10·01	—	—	—	—	—
198—245	—	—	—	0·95	—	—	—	—	—
245—300	—	1·82	—	0·51	—	—	1·82	2·48	0·62
300—405	—	3·71	—	25·08	13·03	12·05	20·71	9·21	2·33
Total ...	26·50	7·64	52·17	101·14	13·03	12·05	22·53	11·69	2·95

Table 2. The sample of η-Al_2O_3 had a surface area of 158 m.^{2}/g., and the amount of acetaldehyde adsorbed on zinc oxide corresponded to an area of 12·1 m.^{2}/g.

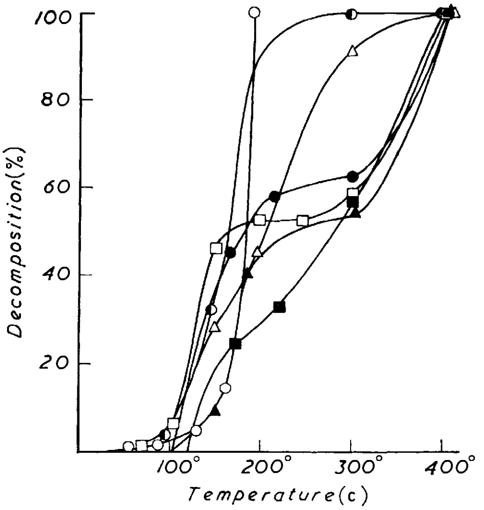
X-Ray diffraction showed that the "AnalaR" sample of alumina had the α-structure (corundum). A sample of cupric oxide from which ethanol had been desorbed was examined by *X*-ray diffraction but no evidence was obtained for the existence of cuprous oxide in the sample.

TABLE 8. *The desorption of acetaldehyde from zinc oxide (molecules/*100 *molecules of acetaldehyde adsorbed).*

Temp. range	$CH_3{\cdot}CHO$	H_2O	$(CH_3)_2CO$	H_2	CO	CO_2	CH_4	C_2H_4	C_2H_6	C_3	1-C_4H_8	n-C_4H_{10}
18°	24·14	4·45	0·67	—	—	—	—	—	—	—	—	—
18—85	1·85	9·87	0·38	0·86	—	—	—	—	—	—	—	—
85—140	0·06	2·76	0·06	0·69	—	—	—	—	—	—	0·11	—
140—195	—	4·51	—	5·95	—	1·59	—	—	—	0·11	0·55	—
195—295	—	4·41	0·33	0·07	—	3·22	0·15	0·27	0·27	0·45	0·72	0·27
295—405	—	7·48	—	8·60	3·65	14·98	9·51	0·39	0·39	1·41	0·17	0·39
Total:	26·05	33·48	1·44	16·17	3·65	19·79	9·66	0·66	0·66	1·97	1·55	0·66

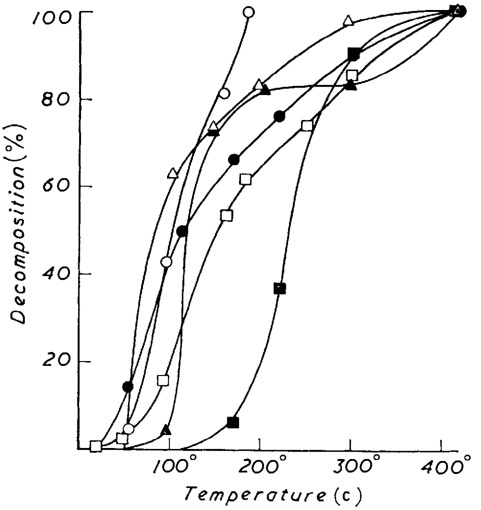
The results of the desorption experiments are summarised in Tables 3—8. Tables 3 and 4 give data about the percentages of the alcohol adsorbed which were recovered as alcohol, the lowest temperatures at which other products were formed, the highest temperature at which the recovery of alcohol was observed, and the total recovery in terms of carbon, hydrogen, and oxygen atoms. The experimental errors in these last figures for the total percentage recovery depended on the cumulative errors in the analyses of all the products collected. No significance should be attached to deviations of less than 10% from the expected recovery of 100%; and for the desorptions from zinc oxide which gave a wide range of products and from α-Al_2O_3 which had a low surface area, deviations of 20% are probably not significant. Tables 5 and 6 show the relative amounts of the various decomposition products formed from each alcohol–oxide system. It was not possible to resolve propane and propene on the 30 ft. phthalate–Celite column used in the early part of the work. However, the C_3 hydrocarbon observed was probably the olefin since no saturated hydrocarbons were formed in the C_2 or C_4 range.

FIG. 1. *The formation of decomposition products from ethanol adsorbed on the oxides. (Percentage decomposition refers to the carbon content of the products formed up to each temperature relative to the carbon content of the total decomposition products.)*



○ CuO. ● NiO. ☐ ZnO. ■ α-Al_2O_3.
△ Anatase. ▲ Rutile. ◐ η-Al_2O_3.

FIG. 2. *The formation of decomposition products from propan-2-ol adsorbed on the oxides. For meaning of symbols, etc., see caption to Fig.* 1.



The data in Tables 3—6 do not indicate the temperature ranges in which the various products were desorbed. With ethanol, the low-temperature fractions contained ethylene, hydrogen, and water; higher hydrocarbons were desorbed next; carbon monoxide, carbon dioxide, and methane were usually only produced at the higher temperatures. A corresponding pattern of behaviour was observed for the products from propan-2-ol except that substantial quantities of acetone were frequently obtained at moderate temperatures whereas acetaldehyde was not observed to any great extent in the products from ethanol. The variation in the extent of the decomposition with temperature for each oxide may be seen from the curves in Figs. 1 and 2, where the extent of the decomposition is given in terms of the carbon atoms in the products expressed as a percentage of the total amount of alcohol decomposed. As an extensive range of products was formed when ethanol was desorbed from zinc oxide, the complete data for this system are given in Table 7. An experiment on the desorption of acetaldehyde from zinc oxide was also carried out and the results of this are shown in Table 8. The percentage recovery of the acetaldehyde was C, 53; H, 73; and O, 103%. In addition to the products shown in Table 8, acetaldehyde over zinc oxide gave rise to two unidentified substances in relatively small amounts at room temperature. The elution times for the peaks corresponding to these substances were 15·1 and 17·6 min. on column C.

DISCUSSION

Nature of the Adsorption.—The surface areas given in Table 2 can only be approximate values because of the assumptions which were made in determining them. Nevertheless, there is agreement between the two sets of values derived from the adsorption of ethanol and propan-2-ol respectively and also the values for the surface area of zinc oxide are in accord with the area of 4·12 m.^{2}/g. determined by the adsorption of n-heptane on a sample of this oxide prepared in a similar manner.[1] The substantial adsorption shown by acetaldehyde on zinc oxide may be due to some polymerisation of the adsorbate or to a greater tendency of acetaldehyde to form multilayers.

The degree of reversibility of the adsorption varies considerably from one oxide to another, as also does the ease of recovery of the alcohol. It is not easy to distinguish between physical adsorption, which will, in part, be due to strong ion–dipole interactions, and chemisorption. Kipling and Peakall[4] have attempted to distinguish between the two types of adsorption on the basis that recovery of the original adsorbate is a feature of physical adsorption. This assumption is unsatisfactory because it ignores the existence of reversible chemisorption which must be occurring to some extent, particularly on α-alumina, anatase, and rutile from which ethanol is recovered unchanged at temperatures as high as 300° (Table 3). It is unlikely that alcohol which remains adsorbed to such high temperature has been only physically adsorbed. Consequently, the correlation of the results with the two types of chemisorption distinguished by Garner[5] is preferable. Alcohol recoverable as such at elevated temperatures is assumed to have undergone reversible chemisorption whereas material only recoverable as decomposition products has been irreversibly chemisorbed, the two types of adsorption probably occurring on different centres. When this distinction is used, it is clear from Tables 3 and 4 that the greatest extent of irreversible chemisorption of the alcohols occurs on zinc oxide and the least extent on anatase and rutile. On each oxide, with the possible exception of cupric oxide, the extent of irreversible chemisorption is slightly greater for propan-2-ol than for ethanol and this may be correlated with the fact that decomposition products from propan-2-ol were formed at lower temperatures than the decomposition products from ethanol on many of the oxides.

The Desorption Products.—The range of decomposition products suggests that the reactions occurring on the oxides are considerably more complex than those which are normally observed in the catalytic decomposition of alcohols at higher temperatures.

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[4] Kipling and Peakall, *J.*, 1957, 834.

[5] Garner, *J.*, 1947, 1239.

The chief reactions in the catalytic decomposition of alcohols at higher temperature are dehydrogenation and dehydration. Consequently, the formation of ethylene, diethyl ether, water, acetaldehyde, and hydrogen from adsorbed ethanol would not be surprising. Similarly, the normal products from adsorbed propan-2-ol would include propene, di-isopropyl ether, water, acetone, and hydrogen. All of these products were, in fact, observed although any given oxide did not yield the complete range of products. More acetone was formed from propan-2-ol than acetaldehyde was formed from ethanol on each oxide. This may be partly the result of a greater ease of dehydrogenation of propan-2-ol compared with ethanol, but it also suggests that acetaldehyde is adsorbed more strongly than acetone and that it is retained on the surface until higher temperatures at which it breaks down to smaller molecules.

The abnormal decomposition products fall into two categories. First, there are the products such as methane and carbon dioxide which must result from the breaking of carbon–carbon bonds in the adsorbed molecules. Secondly, there are the products containing more carbon atoms than the starting material. The presence of a C_4 hydrocarbon amongst the decomposition products from ethanol adsorbed on cupric oxide and zinc oxide is perhaps not surprising as it may result from dimerisation, but the formation of propene from ethanol on nickel oxide and zinc oxide is interesting. These two oxides appear to bring about the formation as well as the rupture of carbon–carbon bonds because they also produced a C_4 hydrocarbon from propan-2-ol.

The high figures for the recovery of oxygen atoms from both alcohols adsorbed on cupric oxide and, to a smaller extent, from the alcohols on nickel oxide indicate one of the reasons why the range of products is more complex than is normally observed in the catalytic decomposition of alcohols. The oxides are behaving as reactants and not merely as adsorbents or catalysts. The excess of oxygen recovered from ethanol adsorbed on cupric oxide corresponds to a reduction of 6% of the oxide to cuprous oxide. Consequently, before considering the decomposition products in detail, it is necessary to examine certain thermodynamic data.

TABLE 9. *Free energy changes for the combustion of ethanol over the oxides.*

Equation	ΔG°_{298} (kcal. mole^{-1})	ΔG°_{673} (kcal. mole^{-1})
$12CuO(s) + C_2H_5OH(g) \rightleftharpoons 6Cu_2O(s) + 2CO_2(g) + 3H_2O(g)$	−159	—
$6ZnO(s) + C_2H_5OH(g) \rightleftharpoons 6Zn(s) + 2CO_2(g) + 3H_2O(g)$	145	83
$6NiO(s) + C_2H_5OH(g) \rightleftharpoons 6Ni(s) + 2CO_2(g) + 3H_2O(g)$	−4·3	−63
$2Al_2O_3(s) + C_2H_5OH(g) \rightleftharpoons 4Al(s) + 2CO_2(g) + 3H_2O(g)$	444	383
$18TiO_2(s) + C_2H_5OH(g) \rightleftharpoons 6Ti_3O_5 + 2CO_2(g) + 3H_2O(g)$	193	140

Thermodynamic Considerations.—Little information is available about the thermodynamic quantities for surfaces and so it is necessary to make use of thermodynamic data for bulk solids. Consequently, the conclusions reached in this section will apply only to reactions involving extensive participation of the oxides as reactants. Two kinds of reaction will be considered—the combustion of the alcohols with reduction of the oxides and the conversion of hydrogen into water with reduction of the oxides.

The combustion of ethanol over the oxides. Free-energy changes for the thermal decompositions of the oxides at 298° K and 673° K were calculated from the data given by Randall *et al.*[6] for cupric oxide and by Brewer[7] for the other oxides. The necessary information on the combustion of ethanol to carbon dioxide and water was obtained from the National Bureau of Standards data.[8] The standard free energies derived for the combustion of ethanol over the oxides are shown in Table 9. The reactions involve an

[6] Randall, Nielson, and West, *Ind. Eng. Chem.*, 1931, **23**, 388.

[7] Brewer, *Chem. Rev.*, 1953, **52**, 1.

[8] National Bureau of Standards, "Selected Values of Thermodynamic Properties," Series I, 1948; Series III, 1949.

increase of four in the number of gaseous molecules, and so the free energies for reactions at low pressures are somewhat lower than the standard free energies given in Table 9. However, this effect is not sufficiently great to alter the conclusion that combustion of ethanol is thermodynamically possible over cupric oxide and nickel oxide, but not over the other oxides in the relevant range of temperature.

Similar calculations for the combustion of acetaldehyde over zinc oxide gave values of ΔG° for 298° K and 673° K of 115 and 68 kcal. mole^{-1} respectively. Thus, although the values are less than the corresponding figures for ethanol the combustion of acetaldehyde over zinc oxide is not thermodynamically possible.

The reduction of the oxides by hydrogen. The standard free energies for the reduction of the oxides by hydrogen are shown in Table 10. These free energies will not be affected by a reduction in pressure from the standard value of 1 atm. since the same number of gaseous molecules appear on both sides of each equation. It is clear that cupric oxide and nickel oxide are the only oxides which can be reduced by hydrogen below 400° C. However, the reverse reaction, *i.e.*, the reduction of water to form hydrogen, is possible over the other oxides if there is any of the metal or lower oxide present.

Detailed Discussion of the Products from the Oxides.—Cupric oxide. The main reaction occurring with both alcohols was combustion to carbon dioxide and water, and these results are in good agreement with the thermodynamic data presented in Table 9. Some dehydrogenation to form acetone occurred with adsorbed propan-2-ol, but no hydrogen was observed. The hydrogen resulting from this dehydrogenation must have been oxidised to water in accordance with the data in Table 10. The failure to detect the presence of cuprous oxide by *X*-ray diffraction in the sample of cupric oxide from which ethanol had been desorbed may have been due to the fact that only a small amount of the reduced form was present

TABLE 10. *Free energy changes for the reduction of the oxides by hydrogen.*

Equation	ΔG°_{298} (kcal. mole^{-1})	ΔG°_{673} (kcal. mole^{-1})
$2CuO(s) + H_2(g) \rightleftharpoons Cu_2O(s) + H_2O(g)$	−29·0	—
$ZnO(s) + H_2(g) \rightleftharpoons Zn(s) + H_2O(g)$	21·5	16·6
$NiO(s) + H_2(g) \rightleftharpoons Ni(s) + H_2O(g)$	−3·3	−7·8
$Al_2O_3(s) + 3H_2(g) \rightleftharpoons 2Al(s) + 3H_2O(g)$	214	200
$3TiO_2(s) + H_2(g) \rightleftharpoons Ti_3O_5(s) + H_2O(g)$	29·6	27·8

Nickel oxide. The behaviour of both alcohols over nickel oxide was similar to that over cupric oxide. The occurrence of combustion, although it was less marked over nickel oxide, and the complete absence of hydrogen from the desorption products are in agreement with the thermodynamic data in Tables 9 and 10. The results differ from those over cupric oxide in two respects. First, partial and complete dehydration to form di-isopropyl ether and propene respectively were observed in the desorption of propan-2-ol. Secondly, there was evidence of a synthetic reaction, producing propene from ethanol and a C_4 hydrocarbon from propan-2-ol. This reaction will be discussed in the next section.

Zinc oxide. Only 26·5% of the ethanol adsorbed was recoverable unchanged. This is in marked contrast to the observations of Kipling and Peakall[4] who claimed that ethanol adsorbed on zinc oxide at room temperature was removed at 60°. Substantial dehydration of ethanol to ethylene occurred below 150° and some ethylene was observed below 67°. However, very much less than the equivalent amount of water was recovered and the only other product in this temperature range was hydrogen. The reaction $Zn + H_2O \longrightarrow ZnO + H_2$ is thermodynamically feasible, provided that zinc metal is available. Zinc oxide normally contains excess of zinc, held interstitially,[9] but only to a limited extent. However, the fact that zinc metal was observed as a condensed film on the cool parts of the

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[9] Bevan and Anderson, *Discuss. Faraday Soc.*, 1950, **8**, 238.

reaction vessel during desorptions from zinc oxide, showed that, in spite of the supposed thermodynamic stability of the oxide, some decomposition to metal was occurring. A similar contradiction of thermodynamic principles has been reported by Player[10] who found that a thin film of zinc oxide on glass could be distilled off at 200° C.

Dehydration, both partial and complete, occurred with propan-2-ol over zinc oxide and a small amount of acetone from a dehydrogenation reaction was observed. More hydrogen and less water were formed than were expected from the relative extents of dehydration and dehydrogenation. This suggests that, as with ethanol, some water was being converted into hydrogen over zinc oxide. The recovery of water from zinc oxide always occurred at substantially higher temperatures than the recovery of the other dehydration products of the alcohols. This is undoubtedly further evidence of the strong adsorption of water on zinc oxide which has been observed previously.[11]

At high temperatures zinc oxide normally acts as a dehydrogenating catalyst.[11,12] However, variable but small extents of dehydration have been associated with differences in the method of preparation of the oxide.[13,14] In the present study, about 50% of the decomposition of ethanol involved dehydration. This is not surprising because, in our work, the oxide was behaving as a reactant and not as a catalyst and, in these circumstances, the strong affinity of the oxide for water would automatically lead to the formation of dehydration products.

The absence of acetaldehyde from the products from adsorbed ethanol on zinc oxide indicates that acetaldehyde was retained very strongly and broken down at higher temperatures to give the observed methane and carbon monoxide and possibly other products as well. Combustion of the alcohols with reduction of the oxides was not expected, nor did the amount of oxygen recovered indicate that the oxide was acting as a source of oxygen. Consequently, the formation of carbon dioxide, observed from alcohols, must have resulted from the decomposition of adsorbed complexes.

The occurrence of a synthetic reaction producing propene from ethanol and a C_4 hydrocarbon from propan-2-ol was marked. Two modes of formation of a C_3 compound from ethanol may be envisaged: (*a*) union of a C_1 complex with a C_2 complex or (*b*) dimerisation of the ethanol with elimination of one carbon atom, perhaps as carbon dioxide. Similar possibilities might account for the formation of a C_4 hydrocarbon from propan-2-ol except that the elimination of two carbon atoms from the dimer would be required. The difficulty about process (*a*) is the nature of the C_2 complex. This might be an adsorbed ethylene residue or an adsorbed acetaldehyde residue. However, ethylene has been shown by Garner and Veal[15] to be reversibly adsorbed on zinc oxide at low temperatures, and ethylene was rapidly desorbed in the present work; so it appears unlikely that sufficient ethylene residue remained on the surface to account for the substantial production of propene which occurred between 300° and 400° (Table 7). Again, smaller amounts of propene were formed from adsorbed acetaldehyde than from ethanol and, consequently, it seems unlikely that an acetaldehyde residue was taking part in the formation of the C_3 compound. Some of the evidence seems to favour the alternative process (*b*) as the source of the C_3 compound. The figures in Table 7 show that C_4 hydrocarbon, C_3 hydrocarbon, and carbon dioxide were formed in the same temperature range and that the production of each increased by roughly the same amount between the ranges 245—300° and 300—405° C.

The variety of products from adsorbed acetaldehyde on zinc oxide shows clearly that this molecule formed a strongly adsorbed complex which tended to decompose in a number of ways at high temperatures. The extent of the desorption of water was in marked

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[10] Player, B.Sc. Thesis, Bristol, 1950.
[11] Taylor and Sickman, *J. Amer. Chem. Soc.*, 1932, **54**, 602.
[12] Zhabrova, Kutseva, and Roginskii, *Doklady Akad. Nauk S.S.S.R.*, 1953, **92**, 569.
[13] Lazier and Adkins, *J. Amer. Chem. Soc.*, 1925, **47**, 1719.
[14] Schwab and Schwab-Agallidis, *J. Amer. Chem. Soc.*, 1949, **71**, 1806.
[15] Garner and Veal, *J.*, 1935, 1487.

contrast to the results with adsorbed ethanol. This may be connected with the fact that the adsorption of the aldehyde was three times as great as that of the alcohol. The production of small amounts of acetone, especially at low temperatures, was interesting. The aldehyde gave rise to smaller quantities of C_3 and C_4 hydrocarbons than the alcohol, and, not unexpectedly, to substantially smaller amounts of ethylene and hydrogen.

Aluminium oxide. The results on η-Al_2O_3 indicated extensive dehydration without any side-reactions and are in good agreement with the usual behaviour of alumina as a dehydrating catalyst. A different range of products was obtained from the alcohols on α-Al_2O_3, which showed some capacity to bring about dehydrogenation as well as decomposition of the alcohols to smaller molecules, and, in the case of adsorbed ethanol, some dimerisation. However, the total extent of the breakdown of ethanol was less over α-Al_2O_3 than over η-Al_2O_3.

Titanium dioxide. Both rutile and anatase showed little tendency to decompose the alcohols. Such reaction as occurred appeared to be mainly dehydrogenation, and it is interesting that acetaldehyde was one of the products from ethanol over both these oxides whereas this compound was always decomposed over the other oxides.

The Effect of Temperature on the Decompositions of the Alcohols.—The curves in Figs. 1 and 2 summarise the way in which the decomposition products are built up as the temperature of desorption is increased. With cupric oxide, combustion of ethanol proceeded so smoothly and readily that no other reaction was possible and a well-defined curve was obtained. A similar curve was also found for the decomposition of ethanol over η-Al_2O_3 which corresponds to the single mode of decomposition by dehydration. However, a definite plateau was present in the plot of the decomposition of ethanol over zinc oxide, suggesting that two distinct processes were occurring on the surface. Reference to Table 7 shows that the first stage corresponds to the formation of ethylene and its co-product, hydrogen, and that this reaction has finished at 200°. Above 250°, the second stage of the decomposition began, showing that a second more stable type of complex was then breaking down. Similar, though less marked, plateaux were found with ethanol and the other oxides.

For propan-2-ol, the graphs are less easy to interpret. Analyses of the products generally indicated a two-stage process, but the different reactions overlapped to such an extent that no plateau was apparent except perhaps for decomposition over rutile. The curves for each alcohol on a particular oxide are similar except that the propan-2-ol decomposed at lower temperatures than did ethanol in most cases. This suggests that more stable surface complexes were formed from ethanol than from propan-2-ol, *e.g.*, acetaldehyde was readily removed only from titania but acetone was desorbed at moderate temperatures from all the oxides.

Further comparison between the behaviour of the alcohols will be made in Part II, in which data relating to the decomposition of higher alcohols will be presented.

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