367. *The Desorption of Alcohols from Metal Oxides. Part II.* The Desorption of t-Butanol and n-Butanol, and the Displacement of Ethanol from Anatase by Propan-2-ol.*

By D. J. WHEELER and C. KEMBALL.

In Part I,* the products formed when ethanol and propan-2-ol were desorbed from a number of oxides were determined. Similar studies have now been made on the desorption of t-butanol from cupric, nickel, zinc, aluminium, and titanium oxides and also on the desorption of n-butanol from zinc oxide and anatase.

The decomposition of t-butanol on each of the oxides occurs at a similar temperature and to about the same extent as does the decomposition of propan-2-ol but the main type of breakdown is dehydration. Some oxidation of t-butanol occurs over cupric oxide.

A variety of products is formed when n-butanol is desorbed from zinc oxide but less extensive decomposition occurs over anatase. As similar results were obtained with ethanol, it appears that there is no substantial influence of chain-length on the manner or the extent of the breakdown which occurs when primary alcohols are desorbed from the oxides.

Measurements of the rate of desorption of ethanol from anatase show that the heat of adsorption varies substantially with coverage of the surface. The displacement of adsorbed ethanol by propan-2-ol occurs much more readily than the desorption of ethanol.

THE first object of the present work was to compare the behaviour of a tertiary alcohol on desorption from a number of oxides with the behaviour already observed in Part I * for primary and secondary alcohols. It was expected that a simpler pattern of decomposition products would be formed from adsorbed t-butanol than from adsorbed ethanol or propan-2-ol because the structure of the tertiary alcohol does not permit any easy type of dehydrogenation to occur. Propan-2-ol was shown to decompose at lower temperatures and to a greater extent than ethanol on most of the oxides used in Part I, and part of the purpose of this work was to see whether this trend continued with the tertiary alcohol. The object of studying the desorption of n-butanol from zinc oxide and anatase was to examine the influence of the chain-length of the alcohol on the extent and the nature of the breakdown of the adsorbed alcohol by comparison with the results obtained previously for ethanol adsorbed on these two oxides.

As the apparatus was suitable for the determination of rates of desorption from an oxide and also of rates of displacement of one alcohol by a second alcohol, it was considered important to carry out some further work on the desorption and the displacement by propan-2-ol of ethanol adsorbed on anatase. Weber and Laidler [1] have reported an interesting example of displacement or " induced desorption." They showed that the presence of light ammonia increased the velocity of desorption of deuteroammonias from an iron catalyst by a factor of about 300. Molinari [2] has suggested that the enhanced rate of desorption results from the transfer of energy from a molecule undergoing adsorption to a neighbouring adsorbed molecule which is then desorbed. He pointed out that his hypothesis would explain some of the relations which have been found between activation energies and frequency factors for a catalytic reaction carried out on a series of different catalysts. Much more experimental evidence is necessary before Molinari's hypothesis can be accepted, because a variation of heat of adsorption with coverage of the surface may be an important factor in determining rates of desorption. The " induced desorption " caused by the presence of a second substance may be a result of keeping the

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* Part I, *J.*, 1960, 332.

[1] Weber and Laidler, *J. Chem. Phys.*, 1951, **19**, 1089.

[2] Molinari, *Z. phys. Chem., Frankfurt*, 1956, **6**, 1.

surface well covered and not of an energy-transfer process. Anatase was chosen as a suitable oxide on which to study rates of desorption of ethanol because no decomposition of the alcohol had been found on this oxide below 100°.

EXPERIMENTAL

Samples of n-butanol ("AnalaR") and t-butanol (B.D.H.) were dried by distillation over anhydrous potassium carbonate. The oxides were prepared as in Part I.

The apparatus for studying the adsorption and the products formed on desorption has been described in Part I. The columns used for the gas-chromatographic analysis of the products were similar to those used previously, with one exception. The sensitivity of the response for n-butanol was inadequate when the 4-ft. column of "dinonyl phthalate" on "Celite" was operated at 33°. Consequently, this column was operated at 82°, a flow rate of hydrogen of 64 ml./min. being used with a pressure difference of 706 mm. across the column. It was necessary to limit the pressures of samples when analysing mixtures containing n-butanol because the vapour pressure of this compound was only about 4 mm. at room temperature.

The apparatus was modified for the experiments on the rate of desorption and the rate of displacement by propan-2-ol of adsorbed ethanol. A second tube to the adsorption vessel was added so that propan-2-ol vapour could be passed over the adsorbent in the displacement experiments. A constant rate of flow of propan-2-ol vapour was obtained by keeping liquid propan-2-ol at 0° and allowing the vapour to flow through a capillary tube, of internal diameter 0·6 mm. and length 40 cm., in the tube into the adsorption vessel.

Samples (100 g.) of anatase (British Titan Products, Anatase H.R.) were used for measuring the rate of desorption of ethanol at 0°, 19·2°, and 37·2°. The oxide was evacuated at 400° and after it had cooled to the required temperature, doses of ethanol vapour were admitted until a small pressure remained above the surface. The total amount of ethanol adsorbed was calculated. Desorption was started by opening a stopcock leading to a U-tube surrounded by liquid nitrogen. The samples collected were removed at intervals and estimated by expanding them into a known volume and measuring the pressure. After the desorption had been studied for about 24 hr., the surface was re-saturated with ethanol, and the rate of desorption measured with propan-2-ol vapour passing through the adsorption vessel. The total amount of each sample collected was estimated as before and the amounts of the two alcohols were obtained by gas chromatography with a 4 ft. column of "dinonyl phthalate" on "Celite" operated at 43° with hydrogen as carrier gas at a flow rate of 57 ml./min.

TABLE 1. *Approximate surface areas of the oxides* ($m.^2/g.$).

Adsorbate	ZnO	CuO	NiO	α-Al_2O_3	TiO_2 (anatase)	TiO_2 (rutile)
t-C_4H_9·OH	3·1	9·9	0·5	0·5	3·6	3·3
n-C_4H_9·OH	3·3	—	—	—	3·4	—

TABLE 2. *Recovery of t-butanol from the oxides.*

Oxide	Alcohol recovered at room temp. (%)	Alcohol recovered total (%)	Lowest temp. for decomp.	Temp. to which alcohol persists	Total recovery (%) C	Total recovery (%) H	Total recovery (%) O
CuO	49·6	69·0	18°	155°	95	99	235
NiO	19·2	29·4	24	104	89	83	103
ZnO	7·4	8·5	18	55	96	92	74
α-Al_2O_3	41·3	71·4	63	223	97	94	93
Anatase	23·8	83·0	46	146	96	96	95
Rutile	25·4	89·8	50	195	93	93	96

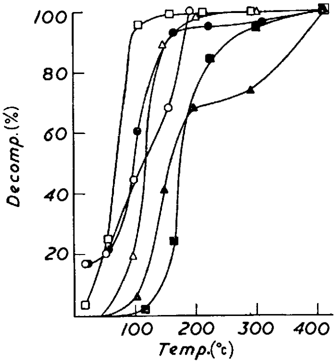
TABLE 3. *Recovery of n-butanol from the oxides.*

Oxide	Alcohol recovered at room temp. (%)	Alcohol recovered total (%)	Lowest temp. for decomp.	Temp. to which alcohol persists	Total recovery (%) C	Total recovery (%) H	Total recovery (%) O
ZnO	5·0	14·9	52°	52°	108	117	132
Anatase	27·8	92·9	17	305	111	111	167

Results.—Approximate surface areas of the oxides are shown in Table 1. These were calculated by assuming that the amount adsorbed at room temperature corresponded to a monolayer on the surface and that the cross-sectional area for the molecules of both alcohols is 20 Å^2.

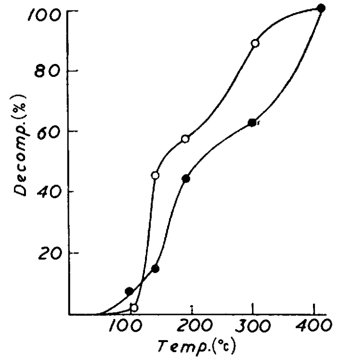
Tables 2 and 3 show the percentages of the amounts of alcohol adsorbed which were recovered at room temperature and throughout the range of temperature over which desorption was studied. The lowest temperatures at which other products were observed, and the highest temperatures at which alcohol was recovered unchanged, are also shown in these Tables, together with the percentage recoveries in terms of carbon, hydrogen, and oxygen of all products. Two of these percentages differ significantly from the expected value of 100%—the value of 235% for oxygen recovered from cupric oxide showing that reduction of the oxide has occurred, and the low value of 74% for zinc oxide indicating that some oxygen has been retained by the oxide. Tables 4 and 5 show the relative amounts of the various decomposition products formed from each alcohol–oxide system. The variations in the extent of the decomposition with temperature for each alcohol on the various oxides are shown in Figs. 1 and 2, the extent of the decomposition being given in terms of the carbon atoms in the products

FIG. 1. *The formation of decomposition products from t-butanol 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.

FIG. 2. *The formation of decomposition products from n-butanol adsorbed on zinc oxide,* ●, *and anatase,* ○.



(For detailed explanation see caption to Fig. 1.)

TABLE 4. *Decomposition products formed from adsorbed t-butanol (molecules/*100 *molecules of alcohol adsorbed).*

Oxide	iso-C_4H_8	H_2O	CO_2	Other products
CuO	10·6	81·0	41·2	$(t\text{-}C_4H_9)_2O$, 2·9; $(iso\text{-}C_4H_8)_2$ 0·4; H_2, 2·0; COEtMe, 3·1; $COMe_2$, 2·4
NiO	51·6	40·2	14·0	
ZnO	87·8	64·3	0·4	
α-Al_2O_3	24·6	16·3	2·9	
Anatase	12·5	12·2	0·05	
Rutile	2·7	4·4	0·8	

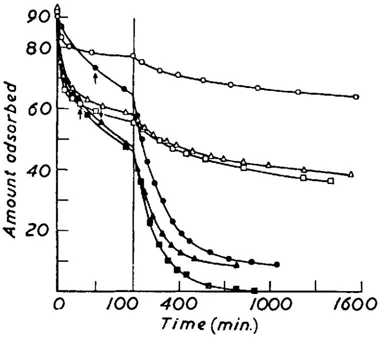
TABLE 5. *Decomposition products formed from adsorbed n-butanol (molecules/*100 *molecules of alcohol adsorbed).*

Oxide	1-C_4H_8	2-C_4H_8	H_2O	n-C_4H_{10}	H_2	CO	CH_4	CO_2	C_2H_4	C_3–	n-C_3H_7·CHO
ZnO	13·6	8·9	11·1	23·0	139·2	14·0	28·0	46·2	2·4	32·0	—
Anatase	—	—	31·5	4·4	2·6	—	—	16·2	—	—	10·3

expressed as a percentage of the total of carbon in the amount of alcohol decomposed over the whole range of temperature.

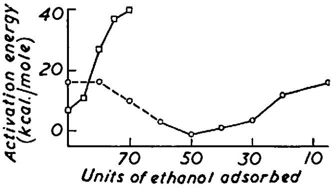
The results for the rate of desorption of ethanol are shown in Fig. 3. The amounts of ethanol adsorbed on 100 g. of anatase were 90·0, 91·7; and 93·0 units at 0°, 19·2°, and 37·2° respectively, where each unit corresponds to a pressure of 1 cm. of vapour in a volume of 100 ml., *i.e.*, approximately 1·23 ml. at N.T.P. The amount taken up by each sample after the desorption of ethanol corresponded to the amount which had been desorbed. When the displacement of ethanol by propan-2-ol was examined there was always a time-lag before propan-2-ol appeared in the samples collected for analysis. The arrows in Fig. 3 indicate the times by which 1 ml. (N.T.P.) of propan-2-ol had been collected. The amounts of propan-2-ol flowing through the capillary tube at the three temperatures were about 17·7, 17·8, and 18·1 ml./hr., respectively, and hence any variations in the rates of displacement were attributable solely to the influence of temperature and not to fluctuations in the flow-rate.

FIG. 3. *The desorption (open symbols) and the displacement by propan-2-ol (filled symbols) of ethanol adsorbed on anatase.*



(Amount adsorbed measured in units corresponding to a pressure of 10 mm. in a volume of 100 ml. at 19°. Circles, 0°; squares, 19·2°; and triangles, 37·2°. Two scales are used to express the time.)

FIG. 4. *The variation with coverage of the apparent activation energies for desorption (squares) and displacement (circles).*



The results in Fig. 3 lead to the following conclusions: (i) Desorption and displacement are substantially slower at 0° than at 19·2°, but both processes are slightly slower at 37·2° than at 19·2°. (ii) The displacement of ethanol occurs slightly more slowly than desorption for the first 20 or 30 min. at each temperature, but at later stages the displacement is much faster than desorption. If it is assumed that no substantial change has occurred in the nature of the adsorbed alcohol between 0° and 19·2°, it is possible to calculate rough values for the activation energies of both desorption and displacement from the rates of the processes at the same coverage at the two temperatures. Activation energies obtained in this way are shown in Fig. 4. The values at high coverages are only approximate because of the difficulty of measuring rates accurately. Likewise, the values at low coverages are subject to error because of the cumulative experimental error in the measurements of the coverages.

DISCUSSION

The approximate surface areas given in Table 1 are similar to the areas found in Part I by the adsorption of ethanol and propan-2-ol (for all the oxides except anatase). Lower areas were obtained for anatase, and this suggests that the larger molecule occupies a greater area than 20 Å^2 or that the structure of this adsorbent has pores which can accommodate ethanol and propan-2-ol more readily than the C_4 alcohols.

As with ethanol and propan-2-ol, the degree of reversibility of the adsorption of t-butanol and n-butanol varied considerably from oxide to oxide. The results provide further evidence for the existence of two types of chemisorption (cf. Garner[3]). Alcohol recovered as such at high temperatures is likely to have been reversibly chemisorbed rather than physically adsorbed, but the proportions of the alcohols which were recovered only as decomposition products must have been irreversibly chemisorbed. The degree of reversibility of the adsorption of t-butanol on each oxide and the temperature range required to desorb the alcohol are similar to the corresponding quantities, observed previously, for the adsorption of propan-2-ol on the same oxides. There is also a general similarity between the results found with n-butanol and the earlier results for ethanol adsorbed on zinc oxide and anatase.

Decomposition Products from t-Butanol.—The main mode of decomposition of t-butanol on all the oxides except cupric oxide was by dehydration to form isobutene and water. The chief factor determining the manner by which this alcohol broke down on the adsorbents was the structure of the molecule and not the nature of the oxide on which it was adsorbed. The structure of the molecule permits dehydration to occur readily but dehydrogenation is only possible if rearrangement of the molecule takes place. Consequently, the range of products formed from the tertiary alcohol was less extensive than the ranges of products formed during the desorption of primary and secondary alcohols. Apart from the formation of small amounts of carbon dioxide at higher temperatures, the only decomposition products observed over the zinc oxide, α-alumina, anatase, and rutile were isobutene and water resulting from the dehydration of the alcohol. The curves, shown in Fig. 1, for the recovery of carbon atoms from the first three of these oxides are well-defined curves because their shape is determined almost entirely by the effect of temperature on the dehydration of the t-butanol. The curve for rutile shows a plateau between 200° and 300° because some of the isobutene was retained up to a high temperature on this oxide and also because a relatively high amount of carbon dioxide was formed on this oxide although the total amount of decomposition was small.

The products obtained from t-butanol adsorbed on cupric oxide differed substantially from the products from the other oxides. The large amounts of water and carbon dioxide formed and the high value for the recovery of oxygen atoms (Table 2) indicate that oxidation of t-butanol occurred over this oxide. A similar behaviour was found with ethanol and propan-2-ol in Part I and, consequently, in the case of cupric oxide, the oxide rather than the alcohol governs the manner in which decomposition occurs. The excess of oxygen recovered corresponded to some 3% reduction of the cupric oxide to cuprous oxide. Some dehydration also occurred on cupric oxide. The small quantity of di-isobutene observed was formed between 18° and 53°, but at higher temperatures only the monomeric isobutene was recovered. The identity of the other compound which was formed at low temperatures was not established with certainty. It was not possible to obtain a sample of di-t-butyl ether in order to measure its retention time in the chromatographic apparatus, but the desorption product gave a retention time closely similar to that for di-isopropyl ether, which would be expected to behave in much the same way as di-t-butyl ether. Two processes governed the shape of the curve in Fig. 1 for the recovery of carbon from cupric oxide—dehydration followed by the more extensive combustion process.

Although the chief mode of decomposition on nickel oxide was by dehydration, there was evidence of some side reactions involving substantial rearrangement of the molecules. The ethyl methyl ketone was formed at room temperature, and the acetone between 55° and 104°. Martineau and Prévost[4] have reported the formation of ethyl methyl ketone from t-butanol over a copper–thorium catalyst. The extent of the decomposition of t-butanol was greater than that of propan-2-ol on nickel oxide, but this was the only case where there was any substantial difference in the reactivity of the two alcohols.

Decomposition Products from n-Butanol.—The experimental error involved in estimating

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

[4] Martineau and Prévost, *Compt. rend.*, 1937, **205**, 154.

the numerous samples collected during the desorption of n-butanol from zinc oxide and anatase was substantial and, consequently, no significance can be attached to the value of 132% for the recovery of oxygen from zinc oxide. However, the higher figure of 167% for the recovery of oxygen from anatase suggests that some oxygen was obtained from the adsorbent. The reduction of the oxide combined with combustion of the alcohol would not be expected to occur to any appreciable extent even at 400°. The standard free-energy change for the reaction:

$$C_4H_{10}O(g) + 36TiO_2(s) \longrightarrow 12Ti_3O_5(s) + 4CO_2(g) + 5H_2O(g)$$

can be evaluated from the data given by Randall *et al.*[5] and Natta *et al.*[6] The values of $\Delta G°$ at 298° K and 673° K are 494 and 285 kcal./mole respectively. As the reaction involves an increase of eight in the number of gaseous molecules, somewhat lower free-energy changes of 430 and 140 kcal./mole would be involved for pressures of 10^{-3} mm. of the reactants instead of the normal standard pressures of 1 atm. As hydrogen was formed, an alternative method of reduction of the oxide may be considered. The free energy change for the reaction

$$3TiO_2(s) + H_2(g) \longrightarrow Ti_3O_5(s) + H_2O(g)$$

was evaluated in Part I and found to be 29·6 and 27·8 kcal./mole at 298° K and 673° K, respectively. However, all these calculations refer to the reaction of bulk solids, and no information is available about the thermodynamic likelihood of surface reactions involving some reduction of the oxide surface.

The behaviour of n-butanol over anatase was similar to that observed in Part I for ethanol. In both cases, the decomposition was slight but some dehydration occurred as well as dehydrogenation. The latter gave aldehyde as one of the products on this oxide whereas aldehyde was always decomposed on oxides other than anatase or rutile. The n-butanal was liberated chiefly between 105° and 140°, and it is significant that a corresponding amount of water was formed simultaneously but no hydrogen. This suggests that some reduction of the surface with oxidation of hydrogen to water was in fact occurring even although the thermodynamic calculations indicate that a bulk reaction of this type would not be expected. The dehydration occurred chiefly between 190° and 305°, and water, carbon dioxide, and hydrogen were desorbed together with n-butane in this temperature range, indicating that the olefin formed by dehydration was being hydrogenated on the surface. The two inflections in the curve in Fig. 2 for the recovery of carbon from n-butanol adsorbed on anatase correspond to dehydrogenation and dehydration respectively.

As with the other primary and secondary alcohols, a complicated pattern of products was obtained from n-butanol on zinc oxide. Dehydration which occurred mainly between 98° and 190° led to the formation of but-1-ene, some of which was isomerized to but-2-ene and some hydrogenated to n-butane. The ratio of the amounts of but-1-ene and but-2-ene was 1·9 in the temperature range 140—190° and it is clear that, although isomerization took place, equilibrium was not established because greater amounts of but-2-ene would have been expected. The amount of water recovered was much less than the total amounts of C_4 hydrocarbons but large quantities of hydrogen were formed. This provides further evidence that the adsorbent can convert water into hydrogen (cf. Part I). Water was only recovered at high temperatures because it was strongly adsorbed, in agreement with the observations of Taylor and Sickman.[7] The large amount of hydrogen recovered showed that dehydrogenation was also occurring but no aldehyde was desorbed. It was retained by the oxide and broken down into smaller molecules above 300°. The complex

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

[6] Natta, Colombo, and Pasquon, " Catalysis," ed. Emmett, Reinhold, New York, 1957, p. 137.

[7] Taylor and Sickman, *J. Amer. Chem. Soc.*, 1932, **54**, 602.

shape of the curve for the recovery of carbon from n-butanol on zinc oxide shows that at least two modes of decomposition were operating. The first rise corresponds to the release of the C_4 hydrocarbons, and the second to the desorption of smaller molecules. Our results on the desorption of n-butanol from zinc oxide differ from those obtained by Rivkin *et al.*[8] for the catalytic decomposition of n-butanol over zinc oxide because they observed n-butanal as a product. The range of products in the present work is similar to the range of compounds obtained by Komarewsky and Stringer [9] when they decomposed n-butanol over an alumina–chromia catalyst.

General Conclusions about the Desorption of Alcohols from Oxides.—It is possible to summarise briefly the main points established in this work and in Part I. The conclusions refer to the four alcohols ethanol, propan-2-ol, t-butanol, and n-butanol and to the oxides cupric, nickel, zinc, α-alumina, η-alumina, anatase, and rutile.

(*a*) Some decomposition of the alcohol is always found on desorption. The extent of this depends mainly on the oxide—zinc oxide gives the most extensive decomposition, anatase and rutile produce the least. (*b*) The secondary and tertiary alcohols are slightly more reactive than the primary alcohols, but chain-length does not influence decomposition appreciably. (*c*) Cupric oxide always causes oxidation of the alcohol with simultaneous reduction of the oxide. (*d*) The predominant type of decomposition of the tertiary alcohol is dehydration. (*e*) The types of decomposition with the other alcohols depend mainly on the oxide and generally include both dehydration and dehydrogenation, and with nickel oxide and, in particular, zinc oxide, further reactions occur. (*f*) The oxides behave as reactants to varying extents—cupric oxide, nickel oxide, and, to a lesser extent, anatase, act as oxidising agents, and zinc oxide shows reducing properties and converts water into hydrogen.

There seems to be a reasonably consistent pattern of behaviour for the desorption of the alcohols from the various oxides and, although more evidence is required before the mechanism of many of the processes can be understood, investigations of this type may help in the understanding of the catalytic action of the oxides at higher temperatures. It is particularly interesting that a number of reactions which normally occur on catalysts only at reasonably high temperature can be brought about under conditions which permit the oxides to function as reactants and not merely as catalysts.

Rates of Desorption and Displacement of Ethanol from Anatase.—One of the most striking results from the rate measurements is the evidence that two types of adsorption of ethanol are occurring on anatase. The rates found at 37·2° for both desorption and displacement are slower than the corresponding rates at 19·2°. This must result from a change in the nature of the adsorption between the two temperatures. The first type of adsorption which occurs at room temperature must include physical adsorption and may also include chemisorption. The second type which occurs at 37° and leads to a more strongly adsorbed alcohol must be chemisorption of an activated kind. The slight increase in the amount adsorbed as the temperature is raised is further evidence that activated adsorption is taking place.

It is possible that the nature of the adsorbed alcohol at 19·2° is not the same as the nature of that adsorbed at 0° because of the existence of an activated process. Consequently, the absolute values of the activation energies shown in Fig. 4 may be in error if the rates at the two temperatures do not correspond to similar states of the adsorbed material. However, the values given in Fig. 4 are useful as a means of comparing the two processes of desorption and displacement and for illustrating the changes resulting from a reduction of surface coverage.

The activation energies for the rate of desorption indicate that the heat of desorption, and likewise the heat of adsorption, must rise steeply as the surface coverage is reduced.

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[8] Rivkin, Nikitina, Paul, and Kulbasova, *Sintet. Kauchuk* (*U.S.S.R.*), 1936, **7–8**, 20.

[9] Komarewsky and Stringer, *J. Amer. Chem. Soc.*, 1941, **63**, 921.

The rise in the activation energy as alcohol is desorbed is the chief factor causing the rate of desorption to decrease with time.

The results during the early part of the displacement experiments must be disregarded. As the flow rate of propan-2-ol vapour was about 17 or 18 ml./hr., 1 ml. (N.T.P.) should have been collected after a few minutes if no propan-2-ol was being taken up by the oxide. The positions of the arrows in Fig. 3 indicate clearly that substantial amounts of propan-2-ol were adsorbed at the beginning of the displacement experiments and, consequently, very little propan-2-ol vapour was passing over the adsorbent at this stage. The relative position of the arrows at 19·2° and 37·2° is further evidence of activated adsorption. The rates of displacement at high coverages relate to a mixture of displacement and desorption perhaps even hindered by the diffusion of ethanol through propan-2-ol. Data obtained after the time indicated by the arrows in Fig. 3 correspond to genuine displacement. Similar considerations apply to the activation energies for displacement in Fig. 4. Only the values relating to a coverage of 60 or less units of adsorbed ethanol were obtained under conditions where a substantial pressure of propan-2-ol was passing over the adsorbent.

Displacement by propan-2-ol occurs more rapidly than the desorption of ethanol alone at all three temperatures. The chief reason for this must be the effect of surface coverage on the heat of desorption. When the surface is maintained highly covered by the incoming propan-2-ol, it is clearly easier to desorb ethanol. This suggests that a substantial part of the variation in the heat of adsorption is due to interaction between the adsorbed molecules, and that the whole of the variation cannot be caused by heterogeneity of the surface. The values for the activation energies for the displacement shown in Fig. 4 are interesting in relation to this point. Little activation is required for displacement for coverages from 60 down to 30 units of adsorbed ethanol but increasing activation is necessary as the coverage is reduced further. It is probable that the rise in activation energy as the last third of the ethanol is displaced is caused by heterogeneity of the surface. The results show clearly that displacement or " induced desorption " is an important method of desorbing a substance from a surface but they do not provide much evidence in favour of Molinari's hypothesis of energy transfer because of the effects of the variation of heat of adsorption or desorption with coverage. The main piece of evidence which may support Molinari's ideas is the negligible activation energy for displacement when 50 units of alcohol are adsorbed compared with the values of over 5 kcal./mole required even at the beginning of the desorption process. However, the negligible activation energy may also be explained by supposing that the differential heat of adsorption of ethanol is reduced to a very small value by the presence of the adsorbed propan-2-ol. It appears that a complete test of Molinari's hypothesis will not be possible until a full-scale investigation is undertaken of both the kinetics and the thermodynamics for the simultaneous adsorption of two substances on the same adsorbent.

THE QUEEN'S UNIVERSITY OF BELFAST.

[*Received, November* 19*th*, 1959.]