case of the other hydroquinones. If a line be drawn as well as possible through the experimental points, with the average slope of the other hydroquinone lines, the pressure at 25° comes out 0.0017 microns.

According to Stelzner[3] the sublimation pressure of hydroquinone at 169°, its melting point, is 14.1 mm. If the pressure curve for hydroquinone, as shown in Fig. 2, is extended to include this datum, the mean slope over the temperature interval involved corresponds to a sublimation heat of 24,000 calories per mole, or slightly less than the 24,800 indicated by the present measurements at ordinary temperatures. This is excellent agreement, for if the specific heat of crystalline hydroquinone exceeds that of its vapor, the heat of sublimation should decrease with rising temperature.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF CAMBRIDGE UNIVERSITY]

THE DECOMPOSITION OF ETHYL ALCOHOL AT THE SURFACE OF THORIA

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Sabatier[2] showed that ethyl alcohol could undergo two important types of decomposition, one to ethylene and water, a reaction promoted chiefly by oxide catalysts, and the other to hydrogen and acetaldehyde promoted by metals. Many catalysts promote both reactions. Contrary to the view of Sabatier, but in agreement with the work of Brown and Reid[3] we have found that thoria prepared by precipitation with ammonia yields approximately equal volumes of ethylene and hydrogen. The surface decomposition, both of alcohol and of formic acid, presents points of interest in that two types of decomposition proceed at the surface of the same catalyst. Two hypotheses have been suggested to explain this fact. On one view[4] the two reactions proceed on the same surface and the proportion of each reaction is determined by the kinetic condition or phase of the molecules that bombard the surface. On the other view, each reaction is promoted by a different type of active area or "patch" of the catalyst surface.[5] There seems to be a certain divergence of opinion as to the

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[3] Stelzner, Landolt-Börnstein-Roth-Scheel, "Tabellen," Julius Springer, Berlin, 1923, 5th ed., p. 1375.

[1] Exhibition of 1851 (England) Scholar at Cambridge, 1924–1925–1926.

[2] Sabatier, *Ann. chim. phys.*, [8] **20**, 326 (1910).

[3] Brown and Reid, *J. Phys. Chem.*, **28**, 1077 (1921).

[4] Hinshelwood, *Proc. Roy. Soc.*, **100A**, 575 (1922); *J. Chem. Soc.*, **123**, 1014, 1333 (1923).

[5] Rideal, *Report Solvay Conference*, Brussels, 1925. Taylor, *J. Phys. Chem.*, **28**, 897 (1924); **30**, 145 (1926). Adkins, numerous papers; see especially THIS JOURNAL, **48**, 1671 (1926).

nature of these active patches. It would appear that Taylor considers the difference in the patches promoting the different reactions to be due to a difference in adsorptive powers which is caused by a difference in unsaturation of individual atoms in or on the regular space lattice of the thoria. Adkins apparently believes that the two types of reaction are determined by different arrangements or spacing of the atoms forming the reactive centers and that these centers do not differ in adsorptive powers. We incline to the view that atomic configuration is an important factor inasmuch as several atoms of the solid appear to be involved in the formation of each type of adsorption complex, but a difference in atomic-surface configuration is always associated with a difference in surface energy[6] and in adsorptive powers. There is, however, *no general* relationship between adsorptive power and catalytic activity, for cases are known where certain poisons are more strongly adsorbed on patches which are relatively inactive compared to others for a catalytic process, and again other cases are known where a poison may be adsorbed in a regular manner and in increasing concentration according to a linear law over a composite surface consisting of patches possessing varying catalytic activities. Frequently, however, it would appear that some one poison, at least, may be found which will be almost selectively adsorbed on the most active patches.

These experiments were undertaken to investigate how much support could be given to this concept of active patches. It is clear that if this view should be correct, the relative rates of reaction should be affected by alteration in the pressure when this is reduced sufficiently to uncover or partly uncover one of the reactive patches, for both reactions are of zero order at ordinary pressures. Finally, it should be possible to bring about the phenomenon of selective poisoning.

Apparatus and Experimental Procedure

The apparatus used for the reaction-velocity and poisoning experiments is shown in Fig. 1. The electrical connections are shown diagrammatically. The source of alcohol vapor is the boiling tube W′ insulated by means of the Dewar flask V′ and heated by means of a coil of Nichrome wire enclosed in a glass tube. The boiling tube is filled through the tube K′ and the residual alcohol removed by suction after each experiment. The alcohol vapor passes through a heated glass tube to the preheating coil N and the catalytic chamber L. The gaseous products of reaction may then pass through the air condenser K and the water condenser H either to the air by bubbling through water at B by means of which a back pressure of about 3 mm. of water is maintained in the apparatus, or to the gas buret F. The excess of alcohol and the condensable products.

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[6] Rideal, "An Introduction to Surface Chemistry," Cambridge University Press, 1926.

of reaction collect in the reservoir I and overflow when the level of the liquid reaches I′. Since most of the condensation takes place in the air condenser at relatively high temperatures, and since the area of contact with the liquid is small, the amount of gas lost by solution in the condensed liquid is reduced to a minimum. Gas samples are collected in the buret F over water saturated with ethylene. The water level is raised to the tap T_2 and the gas sample collected at a constant back pressure of about 3 mm. of water. The water that remains in the capillary U-tube E acts as a manometer. The time employed in collecting a definite volume of gas in the buret is taken with a stopwatch. The gas sample is transferred to the gas-analysis buret through the tube G which is previously filled with water.

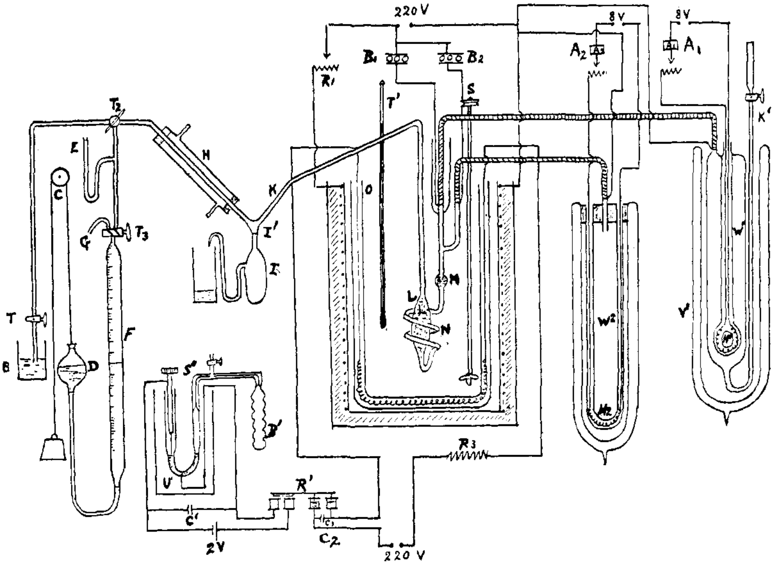

Fig. 1.

An electrically-heated bath of the eutectic mixture of sodium and potassium nitrates was used as a thermostat. Temperatures were read on a nitrogen-filled, mercury-in-glass thermometer which had been calibrated against a standard thermometer. Thermoregulation to 0.5° at temperatures above 300° was obtained by the use of a thermoregulator of special design which operated a relay controlling the internal heating coil D. In view of the difficulty that usually attends high-temperature thermoregulation[7] the arrangement used which proved very satisfactory will be described in detail. The air bulb B′ (Fig. 1) of the form shown to give as large a surface area as possible is placed in the bath and connects through a fine capillary tube heavily lagged with asbestos cord, to a U-tube U′

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[7] Houghton and Hanson, *J. Inst. Metals*, **282,** 173 (1917); **142,** 145 (1915).

containing mercury. The U-tube must be at least 4 mm. in diameter to prevent the mercury from sticking, and it was also found that gentle shaking, by mounting the regulator on the stirrer stand improved the regulation. Electrical connections with the mercury are made by means of platinum wires. A tap sealed into the capillary tubing permits an equalization of the pressure in either arm of the U-tube until the bath is at the desired temperature. The tap is then closed, bringing the regulator into operation immediately. By this means, regulation at different temperatures can be readily obtained. The final adjustment of temperature is made by turning the screw S″.

A second boiling tube similar to the first provides a means of passing volatile poisons over the catalyst through the mixing tube M filled with glass beads.

The alcohol used was carefully purified by shaking with silver oxide to remove aldehydes, distilling and refluxing twice over freshly prepared lime for 24 hours. The use of calcium was avoided owing to possible poisoning effects.

Gas Analysis

The sample of gas collected was transferred to a gas-analysis buret, containing a solution of sodium sulfite saturated with ethylene, which dissolved any aldehyde present. Ethylene was determined by shaking with a saturated solution of bromine in a Hempel pipet. Carbon dioxide was removed by shaking with potassium hydroxide solution, and the hydrogen present determined by explosion with oxygen. The residual gas was shaken with potassium hydroxide solution, and a correction made for the carbon dioxide present as a result of the oxidation of a small amount of ethane that is formed during the course of the reaction. This correction was in every case small. Carbon monoxide was also tested for, but the amount formed was found to be negligible.

Catalyst

The catalytic material used was made by precipitating thorium hydroxide from a hot, dilute solution of thorium nitrate by means of ammonia. A fine, gelatinous precipitate resulted, which was washed until free of electrolytes and was then filtered and dried at 120°.

Results

The average results for the reaction-velocity determinations at several temperatures are given in Table I. Eleven g. of catalytic material was used and alcohol was passed over the catalyst at the uniform rate of 0.2 g. per minute. The reaction was allowed to proceed for half an hour before each determination.

$V_{C_2H_4}$ and V_{H_2} refer to the volumes of ethylene and hydrogen formed,

TABLE I

EFFECT OF TEMPERATURE ON THE REACTION VELOCITY

No.	Temp., °C.	$V_{C_2H_4}$	V_{H_2}
1	297	0.59	0.61
2	307	.93	.88
3	317.5	1.49	1.27
4	326	2.14	1.71

respectively, and are given in cubic centimeters of gas (N. T. P.) per minute. The logarithms to the base ten of the experimental values for the reaction velocities were plotted against the reciprocal of the absolute temperature and yielded straight lines. Values for the temperature coefficient of the velocity constant ξ and for the energy of activation ϵ are calculated from the slopes of these lines.

Calculated in this way, the value of $\epsilon_{C_2H_4}$ is 30,000 cal. and of ϵ_{H_2} 24,000 cal., and the value of $\xi_{C_2H_4}$ 1.58 and of ξ_{H_2} 1.43 for $T = 300°$, where C_2H_4 and H_2 refer to the ethylene and the hydrogen (aldehyde) reactions, respectively.

The two reactions, therefore, have different energies of activation, that for the ethylene reaction being the greater.

Poisoning

As was pointed out before, the two simultaneous reactions may proceed on the same type of surface, the two reactions being determined by the phase of the molecules that bombard the surface, or the two reactions may proceed on different types of active surface. If the former be true, a catalytic poison would not be expected to affect the ratio of the two reactions, although the total amount of the reaction proceeding might be altered. On the other hand, if each reaction is promoted by a different active area, then a catalytic poison might alter the ratio of the reactions provided that the active areas differ in their adsorptive capacities.

The first poison used was water vapor; the result of a single experiment is given below.

Temp., °C.	$V_{C_2H_4}$, cc./min.	V_{H_2}, cc./min.	Water rate, g./min.	Alcohol rate, g./min.
317.6	2.36	2.32	0	0.20
317.6	0.60	1.93	0.02	.20

Water vapor has the effect of cutting down the reaction velocity of the ethylene reaction to a greater extent than the aldehyde reaction. The effect of different concentrations of water vapor is shown in Fig. 2. In every case water vapor has the effect of cutting down the ethylene decomposition to the greater extent. Relatively small amounts of water vapor produce this effect. For the higher concentrations of water vapor, the curves are approximately parallel. This is, no doubt, a simple dilution effect. Another poison, acetaldehyde, was tried in connection with some low-pressure reaction-velocity experiments at 25 mm. and was found to have an effect similar to that of water vapor.

These poisoning experiments, then, indicate that the two reactions do proceed on different active areas, and that the active areas differ in their adsorptive capacities.

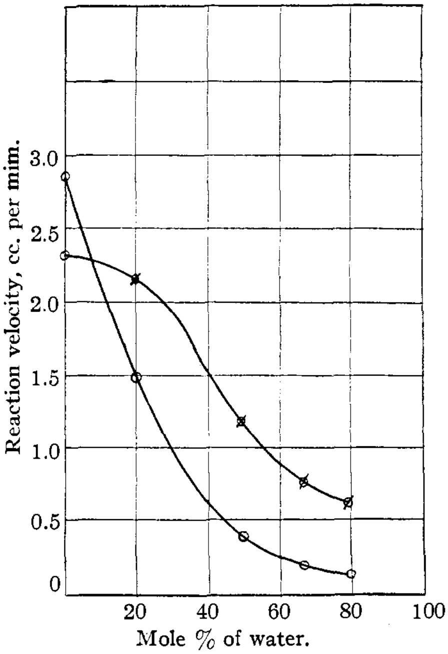

Fig. 2.—○ = ethylene. ∅ = hydrogen.

A third poison, chloroform, was found to behave in a peculiar way. The two previous poisons were reversible poisons, that is, the catalyst quickly regained its former activity when the passage of the poison was discontinued. When chloroform vapor was passed over the catalyst along with the alcohol vapor, there was a very rapid evolution of gas for the first few minutes, which quickly died down to a very low value, and the catalyst became strongly and irreversibly poisoned. The chloroform was therefore added in small quantities, a "whiff" at a time, by connecting the boiling tube to the vapor line for a moment only. Table II shows a characteristic set of results obtained in this way.

TABLE II

EFFECT OF CHLOROFORM ON THE REACTION VELOCITY AT 328°

No.	$V_{C_2H_4}$	V_{H_2}	Chloroform	Remarks
1	1.32	1.01	0	
2	0.92	0.68	Very little	Gas sample after 1 hour
3	10.9	Traces	Slightly more	Sample during rapid gas evolution
4	1.53	0.51[a]		1 hour later
5	1.38	.68[a]		2 hours later

[a] The hydrogen values in Nos. 4 and 5 are not very accurate, due to the small quantity present, but the figures represent the maximum values.

The effect of a very small amount of chloroform is to cut down both reactions. This point will be discussed later. More chloroform produces a very rapid evolution of gas, which is chiefly ethylene. This is apparently due to the chloroform driving off adsorbed ethylene by replacement. However, there also appears to be a promoter effect on the ethylene reaction which lasts for several hours (Expts. 4 and 5).

This apparent promoter effect was studied further by introducing the chloroform in small quantities, placing 1 cc. of chloroform per 100 cc. of alcohol in the boiling tube. The results are contained in Table III.

TABLE III

EFFECT OF CHLOROFORM ON THE REACTION VELOCITY AT 328°

No.	$V_{C_2H_4}$	V_{H_2}[a]	Remarks
1	3.16	0.66	After 1 hour
2	3.10	.54	Half-hour later
3	3.08	.30	Four hours later
4	0.27	.10	5 cc. in 50 in the boiling-tube; sample after 2 hours.

[a] As before, the hydrogen results are only approximate, due to the small amount present.

As compared with the original value for $V_{C_2H_4}$, 1.32 and for V_{H_2}, 1.01, the chloroform has a marked promoter effect on the ethylene reaction, and at the same time poisons the aldehyde reaction. There are three possible explanations of this promoter effect. (1) The chloroform may be driving off adsorbed ethylene. A subsequent investigation of the adsorption of ethylene has shown that the total amount of ethylene adsorbed on 8 g. of catalyst used in this experiment would not be greater than 16 cc. at atmospheric pressure. The excess of ethylene produced is sufficient to account for this in a few minutes, so the effect of the chloroform is not merely one of driving off adsorbed ethylene. (2) The chloroform might cause alcohol molecules that would ordinarily react by the aldehyde decomposition to react by the ethylene method of decomposition. However, this would not account for all the excess of ethylene produced as a result of the presence of chloroform, since the sum of original values for $V_{C_2H_4}$ and V_{H_2}, is less than the promoted value for $V_{C_2H_4}$. (3) Chloroform may have a true promoter effect on the ethylene reaction. This is apparently the case. Norrish and Rideal noted a similar promoter action by oxygen on the reaction of hydrogen with sulfur.[8] It may be assumed that normally a large proportion of the ethylene-producing surface is covered with adsorbed ethylene, and also that chloroform adsorbed on this ethylene-producing surface is capable of promoting the ethylene reaction, but not so well as the thoria surface itself. This accounts for the fact that a very small amount of chloroform poisons the ethylene reaction by being adsorbed on the parts of the surface already producing ethylene. Chloroform does not promote the aldehyde reaction, but poisons it in the usual way.[9]

This promoter action of chloroform is additional evidence for the theory that the two reactions are promoted by different active patches.

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[8] Norrish and Rideal, *J. Chem. Soc.*, **123**, 1689 (1923).

[9] The poisoning effect noted in the presence of small quantities of chloroform may be due to the formation of an unstable chloride at the surface of the catalyst.

Low-Pressure Experiments

As was pointed out above, the action of chloroform in driving off ethylene and then promoting the ethylene reaction indicates that ethylene normally is poisoning the ethylene surface, and possibly also the aldehyde-producing surface and, therefore, the observed temperature coefficients of the reaction velocities may at least in part be due to the temperature coefficient of the rate of evaporation of ethylene from the surfaces. A study of the reactions at low pressures suggests itself as a means of testing this point, for at sufficiently low pressures the surface should be bare of adsorbed gases. Constable found that there was no appreciable change in the reaction velocity with the aldehyde decomposition over copper down to 10 cm. pressure.[10]

Two methods of low-pressure experimentation were tried. By the first method, low partial pressures of alcohol vapor were obtained by saturating a stream of pure, dry nitrogen passing over the catalyst with alcohol vapor. This method proved unsatisfactory as the catalyst rapidly charred so that its activity became greatly diminished. Also subsequent work on adsorption showed that nitrogen is quite strongly adsorbed by the catalytic material. Nitrogen, therefore, is an unsatisfactory diluent for the alcohol vapor.

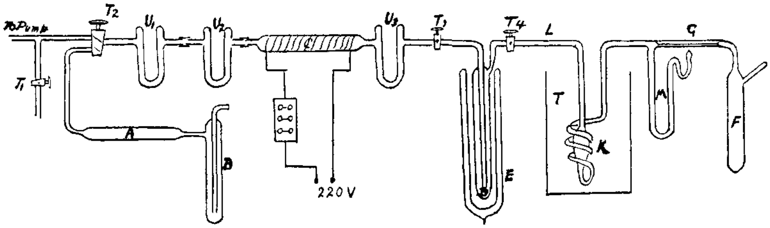

Fig. 3.

The direct method of attack was next employed and proved very satisfactory. The arrangement of the apparatus is shown in Fig. 3. Alcohol is contained in the tube F. G is a length of fine capillary tubing. M is a manometer. The catalyst is contained in the catalytic chamber K placed in the thermostat T. D is a trap which may be immersed in liquid air. U_1 and U_3 are phosphorus pentoxide drying tubes, U_2 a phosphorus pentoxide water-adsorption tube. C contains copper oxide which is heated to about 400°.

The experimental procedure is as follows.

The alcohol in F is frozen by means of liquid air. The system is evacuated with a Hyvac pump capable of maintaining a vacuum of 0.001 mm. The thermostat is then placed in position and brought up to temperature. The pumping is continued for about two hours. The taps T_3 and T_4 are then closed and dry air is admitted to the rest of

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[10] Constable, *Proc. Roy. Soc.*, **107**, 279 (1925).

the apparatus through the drying tubes A and B. The tube U_2 is removed and weighed. If the tube be now replaced and the pumping operation repeated, the weight of the tube does not change by more than a few tenths of a milligram. The adsorption tube is now replaced, the apparatus evacuated and the taps T_3 and T_4 are opened. The trap D is then placed in liquid air and the alcohol in F allowed to melt. The pressure at which the reaction proceeds is controlled by the size of the capillary and the temperature of the alcohol in F. By maintaining constant the temperature of the alcohol, the pressure as read on the manometer remains constant during the course of the determination. The reaction is allowed to proceed for several hours. The taps T_3 and T_4 are then closed, air is admitted to the rest of the apparatus as before and the adsorption tube removed and weighed. The increase in weight represents the amount of water formed from the hydrogen produced by the reaction. The excess of alcohol and the other products of reaction are frozen out in the trap D. This is now removed and the contents brought to room temperature. The gas formed is transferred to the gas-analysis buret by displacement with water, and ethylene determined as before.

The results of the low-pressure determinations are given in Table IV.

TABLE IV

EFFECT OF PRESSURE ON THE REACTION VELOCITY

No.	Temp., °C.	$V_{C_2H_4}$, cc. per hour	V_{H_2}, cc. per hour	Pressure, mm.	Ratio, $V_{C_2H_4}:V_{H_2}$
1	328	2.2	1.1	1	2.0:1
2	328	23.5	11.7 (5)	6	2.0:1
3	318	17.8 (5)	9.3	6	1.9:1
4	318	17.5 (5)	9.0	6	1.9:1
5	328	36.2	18.8	8	1.9:1
6	328	18.6	14.4	8	1.3:1
7	328	25.0	16.2	12	1.5:1
8	328	15.9	10.6	25	1.5:1

No. 6 is the result of an experiment in which the catalyst had been exposed to moist air overnight as usual, and then pumped to 6 mm. only. No. 8 is the result of an earlier experiment and is not so accurate as the other results.

The ratio of the amounts of the two reactions is altered at low pressures from the atmospheric ratio of 1.25 : 1 to 2.0 : 1 at 6 and 1 mm. The relative amount of ethylene is greater at low pressures. This is in agreement with the promoter effect of chloroform discussed previously. Since the ratio of the reactions is the same at 6 mm. as at 1 mm., it may be assumed that the surface is bare of adsorbed molecules at pressures below 6 mm. at 328°, provided that the catalyst has been thoroughly outgassed previously. Expt. 6 shows that if the catalyst be not thoroughly outgassed previous to the experiment, the residual gas or vapor has a poisoning effect on the reaction, cutting down the amount of the reaction and also the ethylene reaction to the greater degree, which was shown to be the usual effect of poisons at atmospheric pressure. The change in ratio of the reactions at low pressures is, therefore, due to the removal from the surface of poisonous materials. Since poisons normally affect the ethylene reaction to the greater degree, the effect of clearing up the surface is to alter the ethylene reaction velocity to the greater extent. This, then, is additional evidence in support of the theory that the two reactions are promoted by different active patches, and that the patches differ in their adsorptive capacities. The ethylene patch is the more strongly adsorbing towards all the poisons investigated. It is significant that the ethylene reaction is also the one requiring the higher energy of activation.

From Expts. 2, 3 and 4, the temperature coefficient of the reaction velocity for the range 318–328° is 1.33 for ethylene and 1.28 for hydrogen at 6 mm. pressure, whereas the atmospheric-pressure values for this temperature range are 1.54 for ethylene and 1.40 for hydrogen. In both cases the temperature coefficient of the reaction velocity is less at 6 mm. than at atmospheric pressure. From this it may be concluded that at atmospheric pressure the reactions are being mutually poisoned by the products of reaction, and that the temperature coefficients observed at atmospheric pressure are partly the temperature coefficients of the rate of evaporation of these products from the surface. The temperature coefficients of the reactions at low pressures may, therefore, be considered the true temperature coefficients.

Supported Catalyst

In order to test the effect of the method of preparation of the catalyst on its activity, a supported thoria catalyst was prepared by the following method.[11]

No. 10-mesh, acid-washed pumice was treated with a concentrated solution of thorium nitrate and the mixture was slowly dried on a water-bath and later in an air oven at 120°. The catalytic chamber was filled with the treated pumice, and dry air was passed over the material at 300° for three hours. The temperature was then slowly raised to 400° and the passage of air continued until it no longer turned litmus red. The catalytic chamber contained 1.5 g. of pumice upon which was supported 0.5 g. of thoria.

The results given in Table V were obtained.

TABLE V

REACTION VELOCITIES WITH A SUPPORTED CATALYST

No.	Temp., °C.	$V_{C_2H_4}$	V_{H_2}	Remarks
1	328	0.56	0.04	
2	338	.82	.09	
3	338	.52	.06	Water 0.2 g. per min.
4	358	.88	.26	

The supported thoria catalyst promotes the ethylene reaction almost exclusively. The amount of hydrogen formed in each case is so small that the analyses are uncertain but, as before, the values given represent possible maxima. Also, the activity of the supported catalyst per gram of thoria is greater than for the unsupported material. For 8 g. of the unsupported material at 328°, $V_{C_2H_4} + V_{H_2} = 2.33$ cc. per min., or 0.29 cc. per min. per g., whereas for the supported catalyst, $V_{C_2H_4} + V_{H_2} =$

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[11] Compare Kramer and Reid, THIS JOURNAL, **43,** 883 (1921).

0.60 cc. per min., or 1.2 cc. per min. per g. of thoria. This increase in the activity may in part be due to an increase in surface area. However, it is significant that this increase in the total activity is associated with a great increase in the activity of the catalyst for the promotion of an ethylene reaction. This might be expected if the two reactions proceed on different active patches, for the ethylene reaction requires the higher energy of activation and is affected most by poisons and so, we suppose, is promoted by the more active patch. An increase in the general activity might therefore be associated with an increase in the number or extent of the more active type of patch. On the other hand, if the two reactions are promoted by the same area, and the reactions depend on a phase relationship of the molecules that bombard the surface, an increase in the activity of the catalyst should increase both reactions proportionally. This, then, is additional evidence in favor of the theory that the two reactions are promoted by different active areas.

As it was pointed out before, water vapor was a temporary poison and no permanent change took place in the catalyst itself. The possibility still remained that the water vapor effected a reversible change in the catalyst, such as oxide $\rightleftarrows$ hydroxide, and that this was responsible for the change in the ratio of the reactions. The supported catalyst is by the method of preparation an oxide catalyst at the beginning of the reactions. From Expt. 3 above it is seen that the effect of water vapor on the supported catalyst is to cut down the ethylene reaction to a greater extent than the aldehyde reaction in the same way that it did with the unsupported catalyst, and there is no increase in the amount of hydrogen formed. It is unlikely, therefore, that the poisoning effect of water vapor is due to any such change in the catalyst itself.

Discussion

The important points brought out in this paper as a result of the investigation of the simultaneous aldehyde and ethylene decomposition of ethyl alcohol on thoria catalyst are as follows.

The two reactions proceed with different energies of activation, that for the ethylene reaction being the greater. Water vapor and acetaldehyde vapor as catalytic poisons cut down the reaction velocity of the ethylene reaction to a greater extent than the aldehyde reaction. Chloroform in relatively small amounts promotes the ethylene reaction and poisons the aldehyde reaction. Excess of chloroform irreversibly poisons both reactions. At low pressures, the ratio of the two reactions is markedly altered. At pressures from 1–6 mm. the ratio of ethylene to hydrogen produced is 2.0:1, whereas at atmospheric pressure the ratio of the reaction velocities of the two reactions is 1.25:1. Above 6 mm. the ratio of the two reactions gradually approaches the atmospheric ratio as the pressure of reaction is increased. The temperature coefficient of the reaction velocity of each reaction is lower at 6 mm. than it is at atmospheric pressure. A supported thoria catalyst prepared from the nitrate by heating in a stream of dry air promotes the ethylene reaction almost exclusively.

The experiments on poisoning, low pressure and supported catalyst have conclusively demonstrated that the two methods of decomposition of ethyl alcohol on the surface of a thoria catalyst cannot be satisfactorily explained by differences either in the kinetic conditions or in the grouping of the molecules that bombard the surface. On the other hand, the theory that the two reactions are promoted by different active areas or patches on the surface has been shown to offer a satisfactory explanation of the observed phenomena. Support for this theory is found from the fact that the two reactions require different energies of activation, that poisons cut down one reaction to a greater extent than the other, that chloroform promotes the ethylene reaction, and that the ratio of the reaction velocities of the two reactions is altered at low pressures.

The points that have been brought out are these: that the reactions proceed on different active patches, and that the active patches differ in their adsorptive capacities, that is, they may be selectively poisoned. Moreover, it seems likely that both the orientation of the surface atoms and the adsorptive power of the active patch play a part in determining the type of reaction that proceeds on the active patch. At atmospheric pressure the reaction velocities depend in part on the poisoning effect of the products of reaction.

Summary

1. The reaction velocities of the ethylene and aldehyde decompositions of ethyl alcohol over thoria have been measured and the energy of activation and temperature coefficient of each reaction calculated.

2. The effect of catalytic poisons on the reactions has been studied and the promoter action of the chloroform is discussed.

3. The effect of low pressures, 1–25 mm., on the reaction velocity has been determined. The proportion of ethylene to hydrogen formed is considerably greater at 6 mm. than it is at atmospheric pressure. The temperature coefficients of both reactions are lower at 6 mm. than at atmospheric pressure.

4. A supported thoria catalyst that promotes the ethylene reaction almost exclusively was prepared.

5. Various theories concerning the nature of the catalytic surface promoting such reactions are discussed. Support is found for the theory that the two reactions are activated by different active patches, and that the active patches differ in their adsorptive powers.

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