THE RATE AND ACTIVATION ENERGY OF THE FIRST ORDER DEHYDRATION OF 2-BUTANOL OVER A COPPER CHROMITE CATALYST

by

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INTRODUCTION

In studies of heterogenous catalysis involving systems of more than one phase, the assignment of a mechanism to a reaction becomes very involved. Since the only place a reaction can occur is at the boundary between the catalyst and the reactant, adsorption and diffusion play an important role in discussions of the system.

Many systems involving a solid catalyst and a gaseous reactant lend themselves most readily to rate studies by using a continuous flow system. Neish (26) has derived equations that are adaptable to continuous flow, heterogenous studies of the type studied here. The first order rate equation of Neish (26) gave satisfactory results, and was used to treat the data taken.

Several authors have reported results of solid catalyst - gas reactant systems where the catalyst seemed to enhance two reactions simultaneously. Although no work could be found dealing with the system studied in this work, parts of the system and similar systems have been studied.

Both Lazier and Adkins (23) and Brown and Reid (8) found that many solid catalysts have simultaneously dehydrated and dehydrogenated 2-butanol. However, no studies of these two reactions of 2-butanol over copper chromite were made. Attempts here were made to classify copper chromite as a dehydrating, a dehydrogenating, or a mixed (both reactions simultaneously) catalyst in a manner similar to Brown and Reid.

Griebstein (18) studied only the kinetics of dehydrogenation of 2-butanol over the copper chromite catalyst, however no reports of the dehydration reaction could be found. A second goal then was to determine the kinetics of the dehydration of 2-butanol over a copper chromite catalyst. Completion

of these studies gave values for the specific reaction rate constant, the activation energy, the entropy of activation, and a comparison of the rate of dehydration to dehydrogenation at several temperatures.

Attempts were made to reverse the reaction studied by Griebstein (18) and from the specific reaction rate constant for the reverse reaction and the mass law calculate the equilibrium constant for the system. Due to analytical difficulties, this study was abandoned in favor of the studies of the kinetics of dehydration as described above.

LITERATURE SURVEY

In the studies of reactions of 2-butanol over a copper-chromite catalyst the most work to date has been on the dehydrogenation reaction. This reaction was extensively explored by Griebstein (18) in his vapor phase kinetic studies of 2-butanol over a copper-chromium oxide (copper-chromite) catalyst. The reaction was found to be of first order with a specific reaction rate constant of 1.10 at a temperature of 576°K. The range of temperatures studied was from 460°K to 620°K and the activation energy was found to be 5,800 calories per mole.

A literature survey was made on the equilibrium studies of the system (2-butanol, 2-butanone, hydrogen). The equilibrium constant was determined over the range of temperatures 438.2°K to 472.2°K by Kolb and Burwell (19), where an effort was made to minimize the deviations of the vapors from ideal gases by using very small pressures.

Cubberley and Mueller (13) determined the equilibrium constant over the temperature range of 445°K to 548°K while taking experimental precautions to reduce the effect of side reactions by using a large amount of hydrogen in comparison with the amounts of 2-butanol and 2-butanone present.

It is worthy of note that the two sets of data agreed very well and when plotted together on the same graph (using equilibrium constant versus temperature) they yielded a single, common curve. There was good agreement in the region where the temperatures of the experiments overlapped.

The purpose of resorting to the equilibrium constant work, was to calculate the reverse specific reaction rate constant by using the mass law. Application of the mass law to the equilibrium constants found in the literature and Griebsteins' values of the forward specific reaction rate constant allowed the calculation of the reverse specific reaction rate constant.

The equilibrium constant study indicated the forward specific reaction rate constant was 14 times as great as the reverse specific reaction rate constant at 576°K. Using the Griebstein value of 1.10 sec^{-1} at 576°K for the forward specific reaction rate constant, the reverse specific reaction rate constant was found to be 0.0786 sec^{-1} atm^{-1}. The value of the equilibrium constant used was taken from a plot of Cubberley and Mueller's data along with the data of Kolb and Burwell (19), where the value of the equilibrium constant was interpolated from the graph at 576°K. The value of the forward specific reaction rate constant was re-determined at 576°K and found to agree quite well with Griebstein's values.

Griebstein found the forward reaction to be unimolecular and first order. It is assumed here that the reverse reaction was bimolecular and second order. The units of the equilibrium constant and the forward specific reaction rate constant combine to produce the units of a second order reaction. The second order rate constant has units of concentration $^{-1}$ $second^{-1}$. In these calculations $atmosphere^{-1}$ is the concentration term, and the units check for a second order reaction.

Exploratory studies were made of the various reactions that are taking place either simultaneously or consecutively and are therefore contributing to the kinetics of the system. Both dehydration and polymerization were found to occur. A series of experiments had been performed by Lazier and Adkins (23 and 2) to show the effect of the structure of the alcohol upon the relative rates of dehydration and dehydrogenation over a zinc oxide catalyst.

In the studies of heterogenous catalysis, where the reaction can take place only at the boundary between the catalyst and reactant, the term surface or contact catalysis is often used. Since this reaction is a gas-solid system the primary interest is at the interface or phase boundary between the catalyst and reactant where adsorption plays an important role. Adsorption is defined as the change in concentration of a gas, liquid, solid, solute, or solvent at the surface of a solid or a liquid as compared to the concentration of the observed material in the bulk of the solid or liquid.

As adsorption plays an important role in this study of heterogenous catalysis, so does diffusion. In some cases diffusion may occur either to or from the catalyst surface or diffusion may occur into or out of the catalyst pores. Very often one of these two diffusion steps will be the rate controlling step of the reaction.

Rigorous equations were derived by Benton (5 and 6) for these heterogenous reactions. However, the general equation is so cumbersome that it is often simplified to three different equations which fit specific cases. These equations are restricted to low conversions (less than 50%). They are characterized as follows: one is for the reactant being strongly absorbed, one is for the product being strongly absorbed, and the third one is for both the product and the reactant being strongly adsorbed. These equations then do not

have general applicability because the absorption characteristics of the reaction systems must be determined before the proper equation can be selected. For this reason Benton's (5) equations were not used for this study.

In heterogenous catalysis studies involving dehydrogenation and dehydration, Brown and Reid (8) have divided the catalysts into three classes, dehydrating, mixed, and dehydrogenating. Adkins and Perkins (3) reported that alumina produces only dehydration, zinc oxide produces both dehydration and dehydrogenation (in about equal amounts) and that copper produces only dehydrogenation.

From these studies it seemed desirable to classify the copper chromite catalyst as to its position, either as a mixed or as a pure dehydrogenating catalyst. Because there is an indication of the formation of a considerable amount of water by the copper chromite catalyst, it is believed by the author, that copper chromite is a "mixed" type of catalyst.

Work of Adkins (1) shows that the method of preparation of a catalyst influences the kind of action as well as its activity. Using this work by Adkins (1), some of the experiments conducted by Griebstein were repeated and retention of activity by the copper chromite catalyst was demonstrated. The catalyst gave the same specific reaction rate constant for the dehydrogenation reaction as obtained earlier by Griebstein.

Brown and Reid (8) indicated the production of CO_2 in all cases except thoria. The catalysts studied by Brown and Reid were blue oxide of tungsten, alumina, thoria, and silica gel. They did not study copper chromite as a catalyst. The origin of the CO_2 is not apparent. It could be the formation of a carbonyl first, then its polymerization to an ester which decomposed to

give CO_2. Also the CO_2 could result from the breaking up of the carbonyl to yield C and CO_2. However, in this work a high boiling fraction was obtained indicating the presence of some esters and other polymers, but no evolution of CO_2 was detected.

Griebstein reported the presence of a high boiling fraction from the liquid products collected as a condensate after the dehydrogenation reaction of the 2-butanol over the copper chromite catalyst. This high boiling fraction was referred to as "homomesityl oxide" and the explanation of its formation is by an aldol type of condensation which yields a hydroxy ketone. The eight carbon hydroxy ketone then loses one molecule of water to become the unsaturated homomesityl oxide. Although several equations can be written to describe this reaction, one of the routes taken by this type of reaction could be:

(1) $C_2H_5-\underset{CH_3}{C}=O + C_2H_5\underset{CH_3}{C}=O \rightarrow H_2O + C_8H_{14}O$; possibly $C_2H_5-\underset{CH_3}{C}=\underset{CH_3}{C}-\overset{CH_3}{C}=O$

In the dehydrogenation reaction this product is found in the material in the collection flask. It amounted to approximately 10 percent of the weight of the reaction products. This heavier fraction was found to be unsaturated by its rapid decolorization of a solution of bromine in carbon tetrachloride without the evolution of hydrogen bromide. The 2,4-dinitrophenylhydrazone indicated the material to be a carbonyl and the melting point of the semicarbozone indicated the material to be a ketone of eight carbon atoms.

When the present studies were started on the dehydration reaction, attempts were made to slow down or to prevent any consecutive reactions such as the one indicated by the production of the homomesityl oxide. The formation of each molecule of homomesityl oxide would produce a molecule of water

from two molecules of ketone formed by dehydrogenation. It was also found that temperature changes from 0°C to 40°C had no effect on the formation of this product. It was found that the length of time the condensate remained in the collection flask had little effect on the amount of water produced. The conclusion drawn from this is that the water was produced at the catalyst bed and not in the collection flask.

A dry ice-acetone trap was used in series, following the ice trap, to see if any low boiling products could be condensed. A condensate was collected in the dry ice-acetone trap and was shown to have a boiling point near 0°C. Using a refrigerated bromine reagent in carbon tetrachloride the condensate was found to be unsaturated. The amount of this low boiling unsaturated compound was quite small, being no more than 1 or 2 percent of the 2-butanol used. Brown and Reid (8) have reported the production of both butene and propene from the dehydration reaction of n-butyl alcohol using silica gel as the catalyst. They report the production of butene was considerably greater than the production of propene. Also, Adkins and Perkins (5) have found butylene in the dehydration of 2-butanol using an alumina catalyst.

Komareswsky, et al (20) have shown that both 1- and 2-butenes were obtained by the dehydration of normal and sec-butyl alcohols, but pure isobutene was obtained from the dehydration of iso butyl alcohol. The catalyst used was phosphoric acid on pumice (pumice treated with 90% H_3PO_4 for 12 hours).

Lazier and Adkins (23) found that the following five primary alcohols (ethyl alcohol, propyl alcohol, isopropyl alcohol, butyl alcohol and iso butyl alcohol) show approximately the same relative activity over a Zn O catalyst as they do over an Al_2O_3 catalyst. The proportion of dehydration to dehydrogenation is apparently independent of temperature. In the case of secondary

butyl alcohol over the temperature range of about 340 - 440°, the proportion of dehydration to dehydrogenation is dependent upon the temperature. The percent of dehydration to total activity (the sum of dehydration to dehydrogenation) is 89 - 71 percent. They have shown the proportion of the two reactions is partially dependent upon the method of preparation of the catalysts. It has also been found that at lower temperatures the dehydration of secondary alcohols takes place with much greater speed with respect to dehydrogenation than it does in the case of the corresponding primary alcohols.

Sabatier and Reid (28) reported that secondary butyl alcohol is attacked by finely divided copper at 160°C and will furnish butanone readily at 300°C without the production of butylene. However, at the lower temperatures there is some tendency to dehydrate and produce some butylene.

Black (7) dehydrated tertiary butyl alcohol over an aluminum oxide catalyst and followed the rate of production of water with a titritimer employing the Karl Fisher reagent. The chemical engineering kinetics were studied employing this procedure and the over-all order of 0.615 was found for the conversion range from zero to 95 percent of the tertiary butyl alcohol to isopropylene.

This reaction was of the heterogenous vapor phase type and involved a volume change. The order was found to be fractional (0.615) and the natural logarithm of the reaction rate is a linear function of the reciprocal absolute temperature over the 100 degree temperature range studied.

The author employed a similar technique to the one employed by Black (7) using secondary butyl alcohol over a copper chromite catalyst instead of tertiary butyl alcohol over an alumina catalyst.

The apparatus used was essentially the same as that employed by Griebstein but with several modifications. The same catalyst was used, as employed by Griebstein, after it had been determined that its dehydrogenating activity had

not changed. The preparation of the copper chromite catalyst is given by Griebstein.

EXPERIMENTAL

Apparatus

The apparatus used was designed to carry out rate measurements on the dehydration of 2-butanol in the gas phase over the solid catalyst copper chromite. Most of the apparatus used was built and used by Cotts (12) and Griebstein (18) in previous kinetic studies. A very good description of the details of construction can be found in Griebstein's thesis where the specifications are all listed in detail. A much shorter and less detailed description that describes the functions of the various component parts is as follows:

Necessary Sections of the Apparatus

(1) A method for introducing the reactant (2-butanol) into the system at a known feed rate.

(2) A method for varying the feed rate as needed with a range that can be changed by at least 100% between the lowest and the highest values.

(3) A method for rapidly vaporizing the alcohol and pre-heating the vapors to the desired reaction temperature.

(4) A method for changing the vaporizer and pre-heater temperature to correspond with the temperature of the reaction tube.

(5) To be able to support a catalyst bed in the reaction tube so that the catalyst can be heated to a known constant temperature.

(6) A method of controlling and varying the catalyst temperature, that is, a method of varying and controlling the reaction tube temperature since the catalyst is supported in the reaction tube.

EXPLANATION OF PLATE I

Description of the apparatus.

A-differentially wound compound motor

B-rheostat motor speed control

C-threaded driving rod

D-50 ml. syringe

E-preheater

F-vaporizer

G-variac, vaporizer temp. control

H_1-oven

H_2-insulation

I-catalyst bed and thermocouple well

J-variac, oven temp. control

K-thermocouple cold junction

L-automatic buret

M-titration cell

N-pyrex glass covered bar magnet

O-magnetic stirrer

P-electrodes

Q-microammeter

R_1-500 ohm resistance

R_2-5,100 ohm resistance

S-switch

T-optical galvanometer

U-potentiometer

V-two way stopcock

W-thermometer

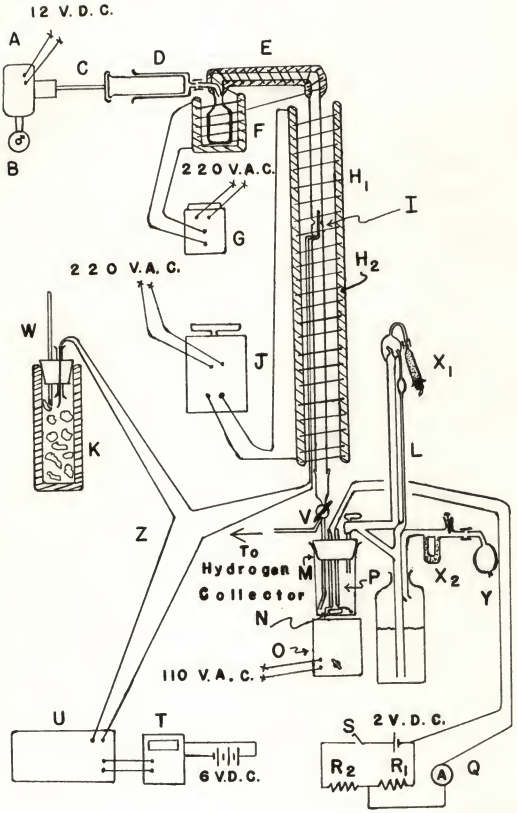
X_1-alumina drying tube

X_2-alumina drying tube

Y-aspirator bulb

Z-thermocouple leads

PLATE I


12 V. D. C.
A
C
D
E
B
F
220 V.A.C.
G
H1
I
220 V.A. C.
H2
W
J
X1
K
L
Z
V
To
Hydrogen
Collector
M
P
X2
Y
N
O
110 V.A. C.
U
T
S
2 V. D. C.
R2
R1
A
Q
6 V.D.C.

(7) A method of measuring the temperature of the reaction, especially the temperature of the center of the catalyst bed during the course of a reaction.

(8) A method of cooling and condensing unreacted alcohol and any higher boiling products formed in the reaction.

(9) A method of continuously analyzing for water as it is produced in the reaction. To be able to analyze the condensate as it is formed or to be able to analyze (scrub) the gaseous products for the water vapor present in them.

(10) A method for removing from the gaseous products all condensable constituents before the gas measured is assumed to be hydrogen.

(11) A method for collecting and measuring the volume of hydrogen gas evolved.

Modifications of Griebstein's Apparatus

A method was devised for cooling and condensing the products of the reaction depending on the particular phase of the problem being studied. For dehydrogenation studies the only condensing action was the reflux action of a tap water cooled condenser in the line of the vapor passage. When the dehydration reaction was being studied by analysis of the condensate, a series of two refluxing tap water cooled condensers was used to increase the efficiency of condensing action. The condensate trap was a three necked one liter flask with two 24/40 standard taper female connections and one 34/45 standard taper female connection. The one liter three necked flask was immersed in an ice-water bath to aid in increasing the efficiency of condensing.

The condensed product material was transferred from the condensate trap to the titration cell through a vacuum system. It consisted of a capillary

two way stopcock drawn out to a fine end for the pick up in the condensate trap and an aspirator to provide the vacuum on the titration cell. This reduced pressure on the titration cell drew the condensed material from the condensate trap to the titration cell where it was titrated for water content with the aid of a standardized Karl Fisher reagent.

An experiment was conducted to ascertain the approximate error in transferring the condensate material. The transferrence error in the apparatus, using only a section of 4 millimeter tubing drawn out to pick up very small volumes, was 15 percent for a five ml. transfer and 75 percent for a one ml. transfer. The error in water measurement is proportional to the error in volume measurement. The quantity of water present is equal to the volume of Karl Fisher reagent times the water equivalence of the reagent, therefore the percentage error for both the volume transfer and the water transfer are the same. The percentage error in the water determination for the capillary transfer was about 5% $\pm$ 1% for transfers of 5 ml., 4 ml., 3 ml., 2 ml., and 1 ml. This error was determined by placing a known volume of 2-butanol that contains a known amount of water in the condensate trap, transferring this with the vacuum system through the capillary tube to the titration cell, then titrating the transferred material with the calibrated Karl Fisher reagent. The results of this operation are then compared with a similar measurement on the same volume of the water-2-butanol mixture added directly to the titration cell. The transfer errors are within the precision of several of the other measurements involved, therefore no further effort will be made to increase the efficiency of the transfer.

Studies were made to determine the amount of time required to complete a transfer of a known quantity of material from the condensate trap to the

titration cell. Only ten seconds were required to transfer ten milliliters of condensate material. No measurement made, in any run, required the transfer of more than ten milliliters of material, therefore this error was considered insignificant compared to the magnitudes of other errors in the study.

The method of continuously analyzing for water as it is produced in the reaction was accomplished by titrating to an electrometric end point using a modified form of the Karl Fisher reagent as described in Mitchell and Smith (24). A diagram of this apparatus may be seen on Plate I. The errors involved in transferring the condensed products are discussed in the previous section. In studying the location of the reaction which produced the water measured, an adaptation was made whereby the condensate trap was eliminated and the vapors passed directly into the titration cell. This is shown on Plate I. The reasons for this adaptation are discussed under the section on catalysts, however, the major change in this operation was the use of a known volume of Karl Fisher reagent and back-titrating it with the vapor products from the reaction tube. This second method of analyzing for water in the vapor form by bubbling the vapors through a known volume of Karl Fisher reagent and using a back-titration electrometric end point will be referred to as "scrubbing" the gaseous products for the water vapor present in them.

Purification of Reactants

The only compound studied in any quantity for this experiment was 2-butanol (Eastman, secondary butyl alcohol). It was dried over calcium carbide and then distilled through a six inch Vigreaux column. The fraction distilling at 98° - 100°C was collected and mixed with approximately 10 percent by weight of the copper chromite catalyst, to remove any possible

catalyst poisons present in the alcohol. After about a week the alcohol was filtered and distilled as before with the 98° - 100°C fraction of the distillate retained for use. The purified 2-butanol was stored in a tightly closed screw cap polyethylene bottle with an arrangement for filling the syringe without opening the bottle or permitting air to enter without going through a calcium chloride drying tube. Some of the 2-butanol was stored in a tightly closed screw cap pyrex bottle and used to compare with the alcohol stored in the polyethylene bottle. No difference was found in the kinetic measurements of the alcohol stored in the polyethylene bottle as compared to the alcohol stored in the pyrex bottle.

An experiment was conducted, very much like the one conducted by Griebstein, to determine the effect of passing 2-butanone through the reaction system just as the 2-butanol had been passed through. The result was to catalyze about ten percent of the 2-butanone to the higher boiling unsaturated ketone (b.p. 160° - 165°C). No gas was evolved during the reaction, but water was present in the reaction flask. This indicates some of the water measured is a result of a condensation reaction and that it is catalyzed by the copper chromite catalyst. The study was made at 300°C.

Because of the experimental work done with 2-butanone, its method of purification is given. 2-Butanone (Eastman, methyl ethyl ketone) was dried over night over anhydrous sodium sulfate. The drying agent was removed by filtration and the ketone distilled through a six inch Vigereaux column. The fraction distilling at 79° - 80°C was collected and either used immediately or stored in a tightly closed screw cap pyrex bottle.

The hydrogen used in the attempted reverse reaction was scrubbed with alkaline pyrogallol, potassium permanganate, a calcium chloride drying tube, and an acetone-dry ice trap as it was being used.

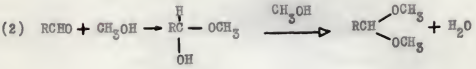
The Method of Water Determination and the Karl Fisher Reagent

A number of ways are available to determine the amount of water present in a given compound or mixture of compounds, however, there are not many methods available to rapidly analyze for water to good precision and accuracy in liquid or vapor form. Only a method using a modified form of the Karl Fisher reagent seemed to be adaptable to this type of study. This method seems to be the most versatile and can handle any quantity of water in organic or in inorganic mixtures. It is rapid and permits a titration study and a "gas scrubbing" study. There are very few compounds that interfere with the Karl Fisher reagent, however low molecular weight carbonyls interfere, and the interference is enhanced by the presence of low molecular weight alcohols.

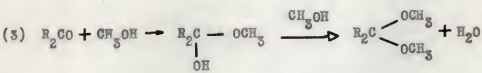
Mitchell and Smith (24) have described a modification of the Karl Fisher reagent as worked out by Smith, et al, (29 and 30). "By greatly reducing the methanol and increasing the pyridine in the regular Karl Fisher reagent, a modified reagent was obtained which reacted normally in the presence of ketones provided that large amounts of the lower alcohols were absent."

Wernimont and Hopkinson (32), employing a similar reagent high in pyridine (84.7 grams of iodine, 288 ml. of pyridine, 33 ml. of methanol, and 64 grams of sulfur dioxide), were able to determine satisfactorily various quantities of water in ten milliliters of acetone by back-titrating excess modified Karl Fisher reagent with standard water solution. The data showed no trend with varying water concentrations, and the results determined were reasonably accurate. Aldehydes, however, still interfered. Their action was characterized by a rapidly fading end point.

The reason carbonyls interfere with the Karl Fisher reagent in water determinations is their tendency to form acetals or ketals by reaction with the methanol of the standard Karl Fisher reagent[1] with the production of additional water as follows:



(2) $RCHO + CH_3OH \rightarrow RC(H)(OH)-OCH_3 \xrightarrow{CH_3OH} RCH(OCH_3)_2 + H_2O$



(3) $R_2CO + CH_3OH \rightarrow R_2C(OH)-OCH_3 \xrightarrow{CH_3OH} R_2C(OCH_3)_2 + H_2O$

The modified Karl Fisher reagent used in this work was the one described by Smith, et al, (30) and again discussed by Mitchell and Smith (24) in their book "Aquametry."

The reagent consisted of 84.7 grams of iodine in 920 ml. of pyridine and 30 ml. of methanol with 45 ml. of liquid sulfur dioxide. A stable end point was obtained by Mitchell and Smith using this modified Karl Fisher reagent on water mixtures of cyclohexanone, acetone, and methyl isobutyl ketone.

A stable end point was obtained when the modified Karl Fisher reagent of Smith, et al, was used here for water mixtures of 2-butanol, water mixtures of 2-butanone, and various combinations of the three, water-2-butanol-2-butanone.

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[1]One liter of standard Karl Fisher reagent contains 84.7 grams of iodine, 269 milliliters of pyridine, 667 milliliters of methanol, and 45 milliliters of sulfur dioxide.

The specifications for compounds used in Karl Fisher reagents are given by Mitchell and Smith. The standardization of the modified Karl Fisher reagent and the calculations for a standard methanol-water solution are given in the Appendix. The modified Karl Fisher reagent used by the author had the following characteristics: The reagent gave the correct value for prepared water-2-butanone-2-butanol mixtures when the reagent was calibrated against a known water-2-butanone-2-butanol standard solution. This experiment was conducted over a wide range of concentrations of water. Solutions prepared by weighing varied in water concentration from 0.5 percent to 20 percent. A linear relationship was obtained when milliliters of reagent were plotted against milligrams of water over the range studied. Large volumes of 2-butanol and 2-butanone solutions were prepared with the ratios of 2-butanol to 2-butanone varying through the following range: 15:85, 35:65, 50:50, 65:35, and 85:15. Known quantities of water were then added by weighing the solutions on an analytical balance. The quantities of water added varied so that at least three different known quantities of water were added to each separate ratio of 2-butanol to 2-butanone. In this way a wide range of various combinations of the three components was prepared and checked with the modified Karl Fisher reagent prepared by the author. Three different preparations of the reagent, all made according to the same ratios of the constituents, were tested on these known standard solutions. Good agreement was found in all cases. The results of this experiment are shown on Plate II. It is therefore concluded that this reagent is specific for water in the system studied.

A positive color change occurs at just slightly past the electrical end point. The end point used was the dead stop electrometric end point as described by Cornish (11), used by Almy, et al, (4), and discussed by Mitchell and Smith (24).

EXPLANATION OF PLATE II

Linear response of Karl Fisher reagent for varying amounts of water in the following mixtures of 2-butanol and 2-butanone.

(1) 15% 2-butanol and 85% 2-butanone

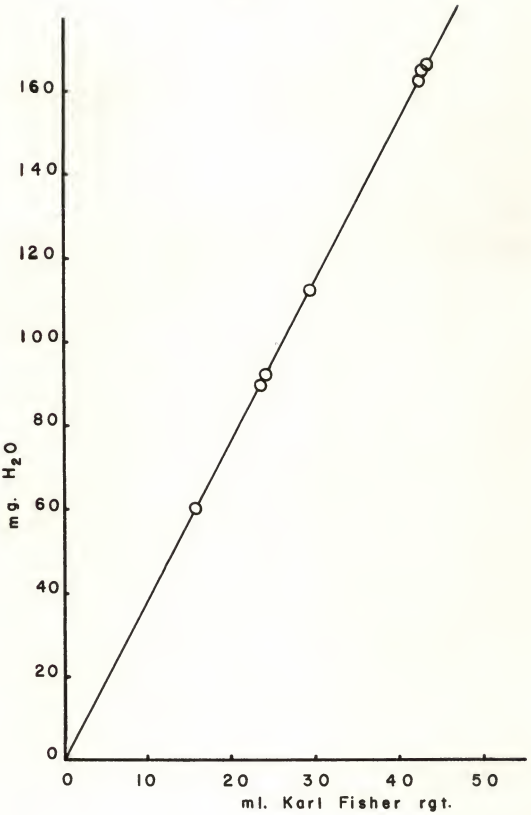
(2) 85% 2-butanol and 15% 2-butanone

(3) 35% 2-butanol and 65% 2-butanone

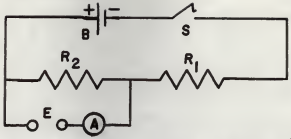
(4) 65% 2-butanol and 35% 2-butanone

(5) 50% 2-butanol and 50% 2-butanone

PLATE II


160
140
120
100
80
60
40
20
0
mg. H_2O
0
10
20
30
40
50
ml. Karl Fisher rgt.

The basic circuit is as follows:



where B = 2 volt battery, S = knife switch, R_1 = 5,100 Ω resistance, R_2 = 500 Ω resistance, A = 0-200 microammeter, E = platinum electrodes.

In this type of titration only one electrode is polarized. As long as water is present, the iodine in the reagent reacts, forming hydriodic acid. Since only reductant is present, the anode remains depolarized and the cathode, polarized, so that no current flows. At the end point, however, the free iodine depolarizes the cathode resulting in a surge of current. This is the description of the forward titration studies. This type of technique was reported as successful with good precision and accuracy by Carter and Williamson (9) and by Cornish (11).

This idea was reversed when the back-titration studies were made. Here the titration cell was fully titrated and a large excess of the reagent was present, usually 50 ml. The water vapor then reacted with the reagent until enough water was formed in excess of the reagent to form hydriodic acid with the iodine in the reagent. When this happens, the anode depolarizes and the cathode polarizes, current flow stops, and the microammeter falls from full scale to zero. It was found that this reverse titration gave a sharper end point than the forward titration for this type of modified Karl Fisher reagent. The full scale swing of the microammeter required only about three to four seconds once the end point was reached, so a very sharp end point could be utilized. This was two to three times as sharp an end point as was obtainable with the forward titration. It was concluded from these experiments

that the end point is both sharp and dependable since the values of a series of runs on any solution tested were reproduced to 0.05 ml. without difficulties due to minor changes of technique.

Plate II indicates that the modified Karl Fisher reagent in the kinetic studies of the dehydration of 2-butanol over a copper chromite catalyst is satisfactory.

Catalyst

The catalyst used for this study was a copper chromite catalyst prepared by Griebstein (18) in his study of the dehydrogenating properties of the catalyst on the same system.

It was prepared according to the method of Connor, et al, (10) and named by them as 37-KAF. As this catalyst is often referred to as "copper chromite,"[1] it will be referred to by this name here. The method of preparation of the catalyst is described by Griebstein (18), also in articles by Connor, et al, (10), by Dunbar (14), by Miyata[2] (25), and by Dunbar and Arnold (15).

The color of the catalyst should be from a brownish black to a black amorphous solid. A green color indicates a large decrease in activity for the dehydrogenation reaction, while the dehydration reaction suffers only a small loss in activity. The activity of the catalyst toward dehydrogenation

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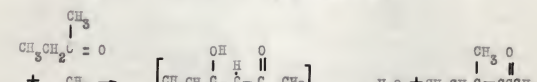
[1] In X-ray diffraction studies of copper chromite by Stroupe (31) no evidence was found for the presence of copper chromite in the "active catalyst," in fact evidence showed the presence of a copper chromium oxide, $Cu_2Cr_2O_4$, not copper chromite, $CuCr_2O_4$.

[2] "Mixed Cu-Cr (27.07 : 32.43) oxide catalyst;" precipitated from an aqueous solution of $Cu(NO_3)_2$ (260) and $(NH_4)_2Cr_2O_7$ (150 parts) by neutralizing with NH_4OH, roasted to a black mass, and after dipping in 10% acetic acid, washed with water and dried at 100°C.

can be destroyed by overheating; a temperature of above 800°K will cause this loss of activity. About 10 percent of the catalyst was barium nitrate; this was added to give the catalyst a resistance to loss of activity on use, and on several occasions nearly a liter of material reacted with no visible loss of activity by the catalyst. This catalyst appears to be extremely stable at or near room temperature if kept dry and out of the sunlight, as was shown by the catalyst's having approximately the same activity for over four years. Within the range of experimental error, the same activity was found with respect to dehydrogenation on the following three occasions: the summer of 1954, the summer of 1956, and the summer of 1957. The approximate date of the catalyst preparation was the summer of 1952 with data being taken on or near the summer of 1953. In all cases listed, the same activity of the catalyst was consistently found toward dehydrogenation. From this evidence it is assumed that the catalyst will remain of constant activity as long as it is dry and used at the same temperature.

In the conclusions of Griebstein's thesis he explains the formation of an unsaturated ketone in the condensate trap. This eight carbon, unsaturated ketone was referred to as a "homomesityl oxide," and an example of the mechanism by which it could have been produced is:



This postulated reaction could explain the formation of the water that has been found with the help of the Karl Fisher reagent.

However, both dehydration and dehydrogenation have been reported from the reactions catalyzed by a large number of substances which indicates copper chromite might dehydrate and dehydrogenate in the same over-all reaction. Such was reported by Lazier and Adkins (23) for Al_2O_3 as a catalyst for 2-butanol, also for 2-butanol over a zinc oxide catalyst (Adkins and Lazier, 2).

If copper chromite were in the "mixed" class, then it should produce water at the catalyst bed and the reaction should not depend on its taking place in the condensate trap. The following results have indicated that the reaction does not take place in the condensate trap.

There was no noted difference in the amount of water produced from such widely different lengths of time as one-half minute to 15 minutes in the time the material remained in the condensate trap before analysis. Also, no difference in the results was found when the temperature of the condensate trap was varied from 0°C to 40° - 50°C. Since the amount of water found apparently does not depend on either the length of time the products of the vapor phase reaction remain in the condensate trap or on the temperature of the condensate trap (within the ranges studied), then it would appear that the reaction that produces the water must be occurring in the catalyst bed. If so, the water would not result from a successive reaction occurring in the condensate trap after the dehydrogenation reaction occurred.

A more conclusive demonstration of the approximate place of the water formation is to eliminate the condensate trap entirely and force the heated vapors to pass directly through the titration cell containing the Karl Fisher reagent and measure the time required to back titrate a known volume of the Karl Fisher reagent. The last design used took the vapors directly

into the titrating cell without time to condense or undergo a successive reaction to form the water as indicated by Griebstein's postulated mechanism. The same kinetic values were obtained when the condensate trap was eliminated entirely as were obtained when it was in use. Therefore the conclusion is that the dehydration reaction took place either simultaneously with the dehydrogenation reaction within the catalyst bed or it goes to completion immediately after leaving the catalyst bed. For the reaction to occur outside the catalyst bed it would have to occur in the vapor phase in a distance of about eight to ten inches when any given molecule has a residence time of only about twenty to thirty seconds after it leaves the catalyst bed before it is titrated by the Karl Fisher reagent.

In Lazier and Adkins (23) study of the ratio of dehydration to dehydrogenation for 2-butanol over a zinc oxide catalyst the following was observed. "The ratio of dehydration to dehydrogenation is relatively independent of the structure of the alcohol as compared with the dependence upon the volume of the catalyst surface. The ratio of the reactions[1] (dehydration to dehydrogenation) with the secondary alcohols (example, 2-butanol) is markedly dependent upon the temperature." In this work effort was made to control the extent of the catalyst surface, that is, to keep the volume of the catalyst constant. In all cases the amount of catalyst used was 5.0000 gm. $\pm$ 0.00009 gm. The "free volume" corresponding to this weight of catalyst was 6.2 ml. $\pm$ 0.1 ml. No further attempts were made to study this aspect of the problem other than to compare runs made at the same temperature and feed rate but with different

---

[1]The dehydration activity of this copper chromite catalyst can be suppressed by the addition of a basic salt such as K_2CO_3 (Lazier, 22).

samples of catalyst all having the same weight. The agreement in this study was very good, rates differing by as little as 0.001 reciprocal seconds were obtained on several comparison runs. This problem was quite thoroughly studied by Garner, et al, (16) for a $ZnO-Cr_2O_3$ catalyst and isopropyl alcohol. He showed that the isopropyl alcohol-$ZnO-Cr_2O_3$ system possesses both dehydrogenation and dehydrating activity. This series of catalysts was prepared by sintering at various temperatures. The results were checked for surface area, structure, and electrical conductance. Cr_2O_3 was found to be a better support than Al_2O_3 owing to its smaller tendency to dehydrate.

Calibration of the Syringe

The rate of delivery of liquid reactant to the system by the syringe was calibrated for various resistances measured with a multimeter, positioned on the ohmmeter scale. In experiments devised to calibrate the rate of delivery of the liquid reactant, on the basis of rheostat settings, a discrepancy was found. The resistance of the spring held contact of the rheostat changed when the rheostat was moved, then returned to the original setting. This difference was found to be quite large if there were two to three weeks difference in the times the runs were made.

A part of this difference was due to corrosion on the wire winding of the rheostat. However, to obtain settings having the same resistance it was found necessary to clamp the contact with an electrically insulated "C" clamp. With this arrangement it was possible to produce settings of the same resistance over periods of time of at least six months.

For work of this nature it is imperative to use a compound wound motor because of its large starting torque and a constant speed under a load. Therefore this type of motor has the characteristics of both the series and

the shunt motors. Because of its series field, it is able to gain speed quickly under a load; and because of its shunt field it maintains an even speed when the load is suddenly taken away or varied. This motor is designed especially for constant speed under quick changes from no load to full load (Nilson and Hornung, 27). From the calibration of the constancy properties of this motor, it was found that a 2 percent error was caused in the reactant delivery rate by a change of 0.1 ohms in the resistance value.

As previously stated, the resistance values were reproduced as often as required for a period of six months. It was necessary to clean the winding of the rheostat of its corrosion. Wiping the winding with a cloth dipped in carbon tetrachloride usually served very well for this purpose.

The syringe was filled with mercury and fastened in place with a small piece of capillary tubing attached with a short section of rubber tubing in exactly the same manner as the vaporizer was attached to the syringe. The capillary tubing was curved upward slightly, to just above the top level of the syringe, to prevent the mercury from spontaneously flowing out of the syringe. The plunger of the syringe was then clamped to the push rod to insure the movement of the plunger as being due only to the motor driven push rod.

The mercury was delivered into weighed receptacles for a measured interval of time at a known resistance setting on the rheostat. The weight of mercury delivered per minute was then converted into milliliters of liquid per minute. The rate of any liquid feedstock in moles per minute could then be calculated. The rate of delivery was found to be constant within one percent throughout the length of the syringe for all resistance settings.

Table 1. Calibration values.

Volts	Resistance ohms	Rheostat setting	ml./min.	Moles/min. 2-butanol
12.0	0.2	0	0.610	0.00665
12.0	1.7	50	0.488	0.00532
12.0	4.0	100	0.445	0.00485
12.0	5.0	I	0.421	0.00459
12.0	6.0	II	0.385	0.00420
12.0	7.5	III	0.311	0.00339

As may be seen from this table, the adjustment of the rheostat permitted the feed rate to be approximately doubled (within 0.013 mole per minute). A wider range of feed rates can be obtained by using different capacity syringes.

RESULTS

Kinetic Measurements

The Calculation of Rates and Order of the Reaction. The method of calculation used for this study was the same as the one discussed by Griebstein in his kinetic studies of the dehydrogenation reaction. It is assumed that the reaction of the secondary alcohol at the catalyst surface to give either a ketone plus hydrogen or an alkene plus water must take place throughout the length of the catalyst chamber. An examination of the equation

(4) $$R-\underset{\underset{H}{|}}{\overset{\overset{R'}{|}}{C}}-OH \xrightarrow{\text{cat.}} R-\overset{\overset{H}{|}}{C}=R' + H_2O \quad \text{or} \quad R=\underset{\underset{H}{|}}{C}-R' + H_2O$$

shows two moles of product are formed for each mole of alcohol reacting. If any of this reaction occurs in the catalyst bed, the space velocity of the product gasses leaving the catalyst bed must be greater than the space velocity of the reactant vapors entering the catalyst bed. This increase takes place not only in the catalyst bed, but also throughout the length of the catalyst bed; thus the space velocities past any two points at different heights in the catalyst bed will be different.

To be able to calculate an average time the unreacted alcohol molecules are in contact with the catalyst, several factors must be known. These factors are:

(1) The free volume of the catalyst bed available for vapors.

(2) The rate of feed of the reactant alcohol.

(3) The temperature of the reaction, especially the temperature of the catalyst bed during the reaction.

(4) A factor involving the molar volume of the gasses.

(5) The rate of change of the alcohol into its products.

Neish (26) has published a mathematical treatment for this type of system, and a part of his work was used by Griebstein. It was also used in this study. The derivation of the equation used is in the Appendix, however, a brief discussion of Neish's (26) work will be given. The fraction of unchanged alcohol emerging from the catalyst chamber is related to the average time of residence of one of the unchanged molecules in the catalyst bed. "k," the specific reaction rate constant, is calculated from this relation. The equation is for a reaction obeying the first order rate law. This equation fits the data obtained from this study. Other equations may be obtained from this equation by substitution of the proper order rate

equation in the derivation. The final equation from the derivation is:

$$(5)\quad k = \frac{2NRT}{V}\left[\ln\left\{\frac{N}{N-n}\right\} - \frac{n}{2N}\right]$$

where k has the units of a number per minute, N is the feed rate of 2-butanol in moles per minute, n = moles of water formed per minute, V = free volume of the catalyst in milliliters, T = temperature in °K, and R = gas constant in ml. atm./deg. mole.

The equation used to calculate k in reciprocal seconds is obtained by evaluating the constants, changing ln to $\log_{10}$ notation and dividing by seconds per minute to give:

$$(6)\quad k_{sec}^{-1} = \frac{2(82.1)NT}{(60\ sec/min)\ V}\left[2.303\ \log\left\{\frac{N}{N-n}\right\} - \frac{n}{2N}\right]$$

or

$$(7)\quad k_{sec}^{-1} = \frac{2.74\ NT}{V}\left[2.303\ \log\left\{\frac{N}{N-n}\right\} - \frac{n}{2N}\right]$$

but, since V is constant for all of these studies and equal to 6.2 ml., then the final equation is:

$$(8)\quad k_{sec}^{-1} = (0.442)\ NT\left[2.303\ \log\left\{\frac{N}{N-n}\right\} - \frac{n}{2N}\right]$$

The temperature is obtained from the thermocouple in the well in the center of the catalyst bed. The moles of 2-butanol, or the feed rate, N, is obtained by calculation from the known volume delivery rate of the syringe, the density, and the molecular weight of the reactant alcohol (2-butanol). The number of moles of water formed, n, was calculated from the volume of Karl Fisher reagent needed to titrate the condensate, the titer or water equivalence of the reagent, the molecular weight of water, and the time needed to collect the condensate titrated. When the second method of water

determination is used where the vapors back-titrate, a known volume of the reagent in the titration cell, only the time required to back-titrate the known volume of reagent, the water equivalence or titer of the reagent, and the molecular weight of water are needed. This calculation gives the quantity, n.

If the dehydrogenation reaction was being studied, the number of moles of hydrogen formed per minute, n, was obtained from the time required to collect 250 ml. of hydrogen in the burette after the necessary corrections were made to dry gas and standard conditions.

The free volume of the catalyst bed, V, was determined by measuring the loosely packed volume of a known weight of catalyst. Five grams were weighed each time the catalyst was changed, and it was the five grams that were transferred to the catalyst bed that were recorded.

The volume of an organic solvent displaced by five grams of catalyst was then measured and the difference between the volume of the loosely packed five grams of catalyst and the volume of the displaced organic liquid was the free volume of the catalyst. The results obtained were quite consistent and amounted to about 85 percent of the loosely packed volume of the five grams of catalyst. Since this term was to be constant throughout the study, its value was assigned, 6.2 ml., and absorbed into a constant term at the start of the final equation.

Determination of the Order of Reaction

The following data were used to provide the experimental determination of the order of the reaction. Since the data fits the first order equation, the specific reaction rate constants were calculated using this equation.

Table 2. First order specific reaction rate constants for the dehydration of 2-butanol over copper chromite catalyst at 576°K.

Feed rate (moles/min.)	T (°K)	k (sec^{-1})
0.00555	576	0.168
0.00555	576	0.169
0.00511	576	0.172
0.00511	576	0.173
0.00446	576	0.166
0.00446	576	0.167
0.00420	576	0.164
0.00420	576	0.164
0.00339	698	0.582
0.00665	698	0.591
0.00665	698	0.578

Table 3. The results of the experimental rate measurements of the dehydration of 2-butanol over copper chromite .

T (°K)	$1/T \times 10^3$	moles/min. of 2-butanol	moles/min. of water	k sec^{-1}	log k
703	1.422	0.00485	0.00232	0.945	-0.025
702.5	1.423	0.00665	0.00372	1.116	0.048
702	1.425	0.00665	0.00284	0.652	-0.186
702	1.425	0.00485	0.00269	0.708	-0.150
701	1.427	0.00339	0.00205	0.794	-0.100
701	1.427	0.00339	0.00181	0.558	-0.253
701	1.427	0.00339	0.00186	0.522	-0.282

Table 3. (Cont.)

T (°K)	$1/T \times 10^3$	moles/min. of 2-butanol	moles/min. of water	k sec^{-1}	log k
700.5	1.428	0.00485	0.00196	0.747	-0.127
700	1.430	0.00665	0.00262	0.625	-0.204
699	1.431	0.00665	0.00256	0.603	-0.220
698.5	1.432	0.00339	0.00166	0.481	-0.318
698	1.433	0.00339	0.00143	0.582	-0.235
697	1.435	0.00665	0.00253	0.591	-0.228
696	1.437	0.00665	0.00249	0.578	-0.238
695.5	1.438	0.00665	0.00246	0.566	-0.249
695	1.439	0.00665	0.00237	0.583	-0.234
695	1.439	0.00665	0.00251	0.537	-0.270
671	1.490	0.00665	0.00262	0.599	-0.223
671	1.490	0.00665	0.00261	0.596	-0.225
669	1.495	0.00665	0.00262	0.598	-0.223
669	1.495	0.00665	0.00308	0.768	-0.115
659	1.517	0.00665	0.00274	0.630	-0.221
650	1.538	0.00665	0.00236	0.499	-0.302
650	1.538	0.00665	0.00239	0.508	-0.294
606	1.650	0.00665	0.000937	0.147	-0.833
604	1.656	0.00665	0.00108	0.171	-0.767
600	1.667	0.00665	0.000954	0.146	-0.836
597	1.675	0.00665	0.000932	0.142	-0.848
593	1.686	0.00665	0.00127	0.203	-0.649
590	1.695	0.00665	0.000898	0.136	-0.867

Table 3. (Cont.)

T (°K)	1/T x 10^3	moles/min. of 2-butanol	moles/min. of water	k sec^{-1}	log k
588	1.701	0.00665	0.000854	0.126	-0.900
586	1.706	0.00665	0.000768	0.113	-0.947
584	1.712	0.00665	0.000904	0.134	-0.873
570	1.754	0.00665	0.000725	0.100	-1.000
558	1.792	0.00665	0.000693	0.095	-1.022
552	1.812	0.00665	0.000586	0.051	-1.292
549	1.821	0.00665	0.000457	0.060	-1.222
508	1.969	0.00665	0.000200	0.023	-1.638
498	2.008	0.00665	0.000120	0.013	-1.886
576	1.736	0.00555	0.00103	0.161	-0.793
576	1.736	0.00446	0.000988	0.162	-0.791
576	1.736	0.00446	0.001009	0.165	-0.783
576	1.736	0.00511	0.000991	0.177	-0.752
607	1.647	0.00665	0.000943	0.146	-0.836
608	1.645	0.00665	0.00140	0.159	-0.799
610	1.639	0.00665	0.00130	0.236	-0.627
649	1.541	0.00665	0.00229	0.477	-0.322
649	1.541	0.00665	0.00200	0.396	-0.402
648.5	1.542	0.00665	0.00194	0.470	-0.328
648.5	1.542	0.00665	0.00196	0.385	-0.415
648.5	1.542	0.00665	0.00227	0.380	-0.420
648	1.543	0.00665	0.00203	0.403	-0.395
648	1.543	0.00665	0.00182	0.349	-0.457

Table 3. (Concl.)

T (°K)	1/T x 10^3	moles/min. of 2-butanol	moles/min. of water	k sec^{-1}	log k
641	1.560	0.00665	0.00220	0.445	-0.352
623	1.605	0.00665	0.00135	0.224	-0.650
623	1.605	0.00665	0.00130	0.220	-0.658
623	1.605	0.00665	0.00168	0.230	-0.638
622	1.608	0.00665	0.00131	0.221	-0.656
621	1.610	0.00665	0.00131	0.219	-0.660
623	1.605	0.00697	0.00177	0.292	-0.535

Calculation of the Activation Energy

Each of the calculated values of k, the specific reaction rate constant, is a separate determination. To obtain the activation energy, E_a, a graph was made with log k plotted versus 1/T. This was done to solve the logarithmic form of the Arrhenius equation.

(9) $$\log k = \frac{-E_a}{2.303R} \cdot \frac{1}{T} + \log A$$

The slope of the best straight line through the points is the activation energy E_a divided by -2.303R. That is:

(10) $$\text{Slope} = \frac{-E_a}{2.303R}$$

To obtain the best straight line, the method of least squares was used, this method places equal weight to every point on the graph. Thus each determination is given an equal weight in determining the slope of the line that

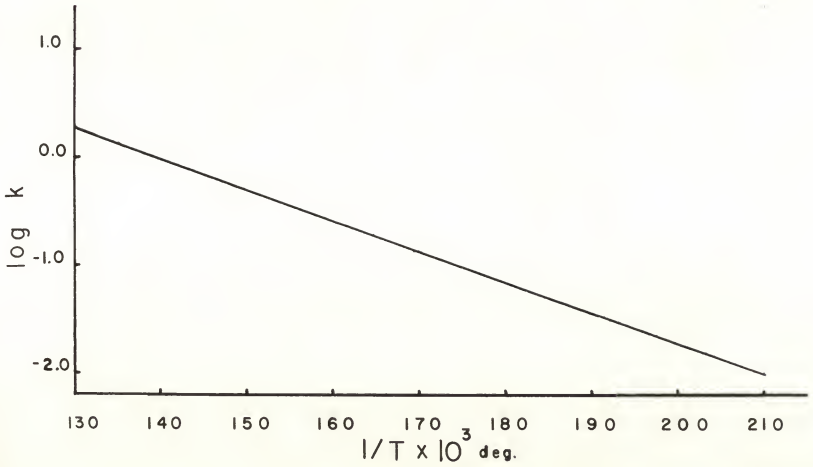
EXPLANATION OF PLATE III

Graphical determination of the activation energy, E_a, for the dehydration of 2-butanol over copper chromite. The method of least squares was used to determine the slope and intercept.

slope = -2.83×10^3 deg.

E_a = 13,000 calories per mole

PLATE III



represents the data. The equations for the least squares calculations are in the Appendix. The slope, as found from the least squares calculation, was -2.83×10^3. Thus: $E_a = (2.83 \times 10^3)(2.303\ R)$

Since R = 1.987 calories/mole-deg., the activation energy, E_a, is 13,000 calories/mole for the dehydration of 2-butanol over the copper chromite catalyst.

The value of A, from the Arrhenius equation, is found from the least squares calculation to be 3.92. Since this value is the logarithm of A, then: $\log A = 3.92$ $\qquad A = 8.32 \times 10^3\ sec^{-1}$

The quantity, A, has often been referred to as the frequency factor, generally it is a much larger value than this, ranging in values from 10^{10} to 10^{13}. Values could have been found for A by substituting the value of E_a into the Arrhenius equation

(11) $k_{sec^{-1}} = A\, e^{-E_a/RT}$

and solving for A when values are substituted for k, T, and R. Also the same result can be obtained by extrapolating the curve on Plate III to $1/T = 0$ and reading off the intercept on the log k axis.

Writing the Arrhenius equation in its final form by substituting the values calculated from the data, gives:

(12) $k_{sec^{-1}} = 8.32 \times 10^3\ sec^{-1} \exp\left[\frac{13{,}000\ cal/mole}{RT}\right]$

Absolute Reaction Rate Calculations

To calculate the entropy of activation, $\Delta S^{\ddagger}$, the following quantities must be known or evaluated: the rate of the reaction, k; the temperature, T; and the energy of activation, E_a. The value of G, the transmission coefficient, is assumed equal to one. In the equation

(13) $k = G \frac{kT}{h} \exp\left[\frac{-\Delta H^{\ddagger}}{RT}\right] \cdot \exp\left[\frac{\Delta S^{\ddagger}}{R}\right]$

k is the Boltzman constant and h is Planck's constant. Assume $\Delta H^{\ddagger}$ to be E_a and G = 1, as stated above. Then rewriting the equation:

(14) $\Delta S^{\ddagger} = \frac{E_a}{T} + 2.303R (\log h + \log k - \log k - \log T)$

Using the previously determined values of k and T, the values are calculated for $\Delta S^{\ddagger}$ for the dehydration reaction of 2-butanol over a copper chromite catalyst. The values calculated are:

Table 4. Entropy of activation.

T (°K)	$\Delta S^{\ddagger}$ (e.u./mole)
700	-47.19
650	-46.03
600	-46.65
550	-46.28
500	-46.76
ave.	-46.58

Discussion

An explanation of the highly negative value of the entropy of activation for the dehydration of 2-butanol over the copper chromite catalyst can be given in terms of the configuration of the activated state. If the activated state is a state of high organization, then it has a low probability of existence. In order to have high organizational requirements placed on the activated state, it is necessary to require orientation of the molecules when they are

adsorbed on the surface of the catalyst. A part of this requirement can be satisfied by postulating the mechanism for the formation of the "homomesityl oxide" as being one of the products of the activated state. That is the activated state is a dimerization and the unsaturated eight carbon ketone is a product of the activated state that most nearly resembles the activated state itself.

In any discussion of a catalyst of this type, availability of reaction sites must be considered. Glasstone, et al, (17) has calculated the number of possible sites on a catalyst surface to be as many as 10^{15} sites per square centimeter. Griebstein (18) used the value of 100 to 300 square meters per gram as the surface area of the copper chromite catalyst. Using 10^{15} sites per square centimeter and 200 square meters per gram for the copper chromite catalyst, then five grams of catalyst would contain $5 \times 200 \times 10^4 \times 10^{15} = 10^{22}$ sites.

This value was taken to be about 1/60 mole of sites. Since five grams of 2 $CuO.Cr_2O_3$ has 8.7×10^{22} atoms of all types, then one atom in every nine atoms present in the catalyst is an active center. This means even more of the atoms in the surface are active centers, in fact nearly every atom on the surface is a potential site for a reaction.

In discussing a typical reaction where the rate measurement of water produced indicated 0.00372 moles of water was produced per minute at 702.6°K when a feed rate of 0.00665 moles of 2-butanol were charged into the catalyst bed. An entering molecule of 2-butanol can reside in the catalyst bed only about one second if it fails to react. If the two rates are converted to units of seconds, we have: 0.62×10^{-4} moles per second of water formed and 1.11×10^{-4} moles per second of the 2-butanol reacting all in one second.

The result of this is 0.373×10^{20} or 3.73×10^{19} molecules of 2-butanol dehydrated by 10^{22} sites in one second.

If a "sit down" time of one second be postulated for a molecule on a site, then only one in 200 sites would be in use. Also, if all sites were considered equally active, then each site will cause a reaction only once every 200 seconds.

However, Griebstein also made a similar calculation for the dehydrogenation reaction, and since the two reactions are somewhat similar, then there are two reactions, each using one site for each 200 sites available.

If the "sit down" time were increased to two seconds or if the desorption reaction from the catalyst were the limiting step in the reaction sequence, then these sites would be tied up. Also if the size of a bulky alcohol molecule or the even bulkier "homomesityl oxide" were to adsorb on a catalyst site, then they might mask a large number of sites in the immediate area where they are adsorbed. Using these ideas to approximate, say a single bulky molecule could mask 20 other sites and allowing for some of the sites to be unavailable due to a stearic type of interference, it is not too difficult to use up these extra active sites.

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APPENDIX

Standardization of the Karl Fisher Reagent

Based on the book "Aquametry" by Mitchell and Smith (24), the following are illustrative calculations of typical determinations of water produced in the reaction. As a basis, in making this standardization, it is desired to have ten milliliter portions of a solution contain about 150 milligrams of water. This usually gives a titer of about 40 ml. to 80 ml. of the Karl Fisher reagent.

I. Preparation of the methanol-water standard.

A. To prepare one liter of the standard, take a dry one liter, glass stoppered volumetric flask. Fill the flask to within about 100 ml. of the mark with dry methanol (<0.1% water) and keep at 25°C, if possible.

B. Take a smaller dry flask containing about 200 ml. of the same methanol. Weigh about 15 grams of distilled water into the liter flask and adjust the volumetric flask to the mark with the methanol from the smaller flask.

C. When the flask is adjusted to the mark at 25°C with the weighed water (about 15 grams) in the 1000 ml. methanol, the standard has been prepared.

II. Standardization of the standard (water in methanol) solution and the standardization of the Karl Fisher reagent.

A. Titrate several 25 ml. samples of the dry methanol (about 5 or 6); continue to titrate samples until good agreement is reached.

B. Titrate 3 or 4 (later maybe 2 will be enough) of the prepared standard water-methanol solution. (Use 10 ml. samples).

C. In both A. and B. above, the unstandardized Karl Fisher reagent has been used.

D. In making the titrations, always add a small amount of dry methanol to the cell first and titrate it, so the end point is determined from a freshly titrated cell.

E. Be sure to correct for this added reagent that is titrated in addition to the sample that is titrated for water. The sample refers to the standard solution.

F. The net titers should check to within 0.1 ml.

G. The total water content of the standard and the water equivalence of the Karl Fisher reagent is calculated as follows: Let a = ml. of Fisher reagent required to titrate the volume of methanol added to each flask to compensate for the adsorbed moisture. Let b = ml. of Fisher reagent required to titrate the volume of methanol added to each flask to compensate for adsorbed moisture plus the 25 ml. sample (of dry methanol). Then, b - a = c = ml. of Fisher reagent required to titrate the 25 ml. sample of dry methanol. d = ml. Fisher reagent required to titrate 9.85 ml. of the dry methanol. This value is calculated by proportion from the value of c, the average titer of 25 ml. of the standard solution. (For practical purposes, 10 ml. of the dry methanol contains 9.85 ml. of methanol and 0.15 ml. of water). e = average ml. of reagent required for titration of several 10 ml. samples of the standard water solution. (Correct for the adsorbed moisture on the walls of the flask). f = known mg. of water added to the 10 ml. of the water standard. Then, e - d = ml. of Fisher reagent required for f alone and

f/ (e - d) = g = mg. of water equivalent to one ml. of Fisher reagent. Finally, j = f + (g x d) = mg. of water in 10 ml. of standard water-methanol solution. If, (g x d) = k, then, j = f + k is the solution to this problem.

Derivation of the First Order Rate Equation

The first order rate equation as derived by Neish, used by Griebstein, and again in treatment of this data is derived as follows:

Let N be the moles/minute of reactant alcohol (2-butanol) entering the catalyst chamber and let n be the moles/minute of hydrogen formed.

Then $V_m \frac{(N+n)}{N}$ is the volume of gas/minute flowing past any point in the catalyst chamber when V_m is the molar gas volume.

The flow in ml./minute multiplied by the time of flow, dt, must equal the free cross-sectional area of the catalyst chamber times a unit of length, dx. Thus

(15) $V_m \frac{(N+n)}{(N)} \quad dt = A\,dx$

Assuming a perfect gas at one atmosphere pressure

(16) $V_m = NRT$

where R is the molar gas constant in units of ml. -atmospheres and T is the absolute temperature.

For a first order reaction the rate may be expressed as

(17) $\frac{dn}{dt} = k(N - n)$

where again N is the number of moles of reactant originally present and n is the number of moles of product formed.

Substituting the values for V_m and dt obtained from equations (16) and (17) into equation (15) it becomes, at one atmosphere pressure for a first order reaction.

$$(18)\quad NRT\ \frac{(N+n)}{N}\ \cdot\ \frac{1}{k(N-n)}\ dn = Adx$$

Integrating over the length of the catalyst bed equation (18) becomes

$$(19)\quad \frac{NRT}{k}\left[\int_{n=0}^{n=n} \frac{(N+n)}{N(N-n)}\ dn\right] = \int_{x=0}^{x=x} Adx$$

but

$$(20)\quad \int_{x=0}^{x=x} Adx = V$$

where V is the free volume in ml. of the catalyst bed available for gas flow so that equation (19) becomes

$$(21)\quad \frac{NRT}{k}\left[\int_{0}^{n} \frac{(N+n)}{N(N-n)}\ dn\right] = V$$

By application of the method of partial fractions equation (21) may be written

$$(22)\quad \frac{NRT}{k}\left[\int_{0}^{n} \frac{-dn}{N} + \int_{0}^{n} \frac{2}{(N-n)}\ dn\right] = V$$

and the integration is now readily carried out to give

$$(23)\ \frac{NRT}{k}\left[-\frac{n}{N} - 2\ln(N-n)\right]_0^n = V$$

Evaluation at the upper and lower limits gives

$$(24)\ \frac{2NRT}{k}\left[\ln\left\{\frac{N}{(N-n)}\right\} - \frac{n}{2N}\right] = V$$

Solution of equation (24) for k gives

$$(25)\ k = \frac{2NRT}{V}\left[\ln\left\{\frac{N}{(N-n)}\right\} - \frac{n}{2N}\right]$$

where k has the units of a number per minute since N is in moles per minute.

The Method of Least Squares

The least squares line for a given set of experimental data was obtained by use of a set of normal equations based on the equation of a straight line. Using the slope intercept form $y = mx + b$ where m is the slope and b is the intercept, the evaluation is made by summing over all points.

Using the equations $\sum y = m\sum x + Nb$ and $\sum xy = m\sum x^2 + b\sum x$ as derived in Mellor and solving these two equations simultaneously gives values for m and b, as follows:

$$b = \frac{\sum x \sum xy - \sum x^2 \sum y}{\left[\sum x\right]^2 - N\sum x^2} \qquad m = \frac{\sum x \sum y - N\sum xy}{\left[\sum x\right]^2 - N\sum x^2}$$

By substituting the values from Table 3 into these two equations, e.g., $x = 1/T \times 10^3$ deg. and $y = \log k$ and making the appropriate calculations, both the slope and the intercept of the best straight line representing this kinetic data can be obtained. In making these calculations it is suggested to use a four column table, the headings of which could be: x, x^2, y, and xy.

From these four columns and the value of N, all terms of the b and m equations solved can be evaluated separately. The values obtained using data from Table 3 for the new four column table are: $N = 54$, $\sum x = 85.1$, $\sum x^2 = 135.1$, $\sum y = -29.2$, $\sum xy = -48.8$. Combining these values to conform to the equations for b and m gives: $\sum x \sum y = -2485$, $N \sum xy = -2635$, $\sum x \sum xy = -4153$, $\sum x \sum xy = -4153$, $\sum x^2 \sum y = -5945$, $\left[\sum x\right]^2 = 7242$, $N \sum x^2 = 7295$. Upon introduction of these values into the appropriate equations for slope and intercept gives values of: m = slope = -2.83, and b = intercept = 3.92. That is, the slope of the plot of $1/T \times 10^3$ deg. versus log k is -2.83×10^3 deg. and the intercept is 3.92. The activation energy is calculated from the slope and the value of the "A" term of the Arrhenius equation is calculated from the intercept value.

THE RATE AND ACTIVATION ENERGY OF THE FIRST ORDER DEHYDRATION OF 2-BUTANOL OVER A COPPER CHROMITE CATALYST

by

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The dehydration studies of 2-butanol over a copper chromite catalyst were studied using a continuous flow system. The rate of water production was followed using a modified Karl Fisher reagent, as given in Mitchell and Smith, with an electrometric titrimeter. To complete a rate measurement, the time necessary to back titrate a known volume of Karl Fisher reagent was recorded. Using the water equivalence of the reagent, the amount of water produced was then calculated.

Specific reaction rate constants were found using a first order kinetics equation as derived by Neish (Can. Jour. Research 23-B:46-69. 1945). At temperatures less than 540°K no measurable reaction was noted, but with the temperature of 576°K a first order reaction was observed with a rate constant of 0.166 sec^{-1}, and was found to be independent of the concentration of 2-butanol by varying the feed rate of 2-butanol by 100 percent. An activation energy of 13,000 cal. per mole was calculated from the slope of the best straight line representing the data plotted as $1/T \times 10^3$ deg. versus log k. The slope of the best straight line was found by the method of least squares. The intercept of this plot gave the frequency factor (A) of the Arrhenius equation, this value was 8.32×10^3 sec^{-1}. From the activation energy, calculations were made for the entropy of activation for the temperature range of 500° to 700°K. The average entropy of activation was -46.6 e.u. $\pm$ 0.6 e.u., assuming the transmission coefficient equal to unity.

Griebstein reported a value of 5,800 cal. for the dehydrogenation of 2-butanol over a copper chromite catalyst, and 17,500 cal. for the same reaction over a nickel-chromium oxide catalyst. This was a first order reaction between 450° and 620°K. Griebstein's entropy values and frequency

factors were, respectively, -49.7 e.u. $\pm$ 0.3 e.u., 1.4 x 10^2 sec^{-1} and -31.0 e.u. $\pm$ 0.1 e.u., 2.1 x 10^6 sec^{-1} for the two reactions described above.

The value of 13,000 cal. for the activation energy of this reaction is somewhat smaller than the values normally expected from uncatalyzed reactions. However, it is of the right order of magnitude for many catalyzed reactions. Kotelkov reported 10,000 cal. as the activation energy of the dehydrogenation of isopropyl alcohol over an activated, furfural waste, catalyst. He found the reaction was first order in the temperature range of 300° to 400°K. Similar values reported by Kotelkov are: 15,600 cal. for the same reaction over a dendrite catalyst, and 16,900 cal. for this reaction over an activated industrial carbon catalyst formed from the decomposition of organic compounds.