

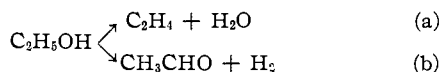
[CONTRIBUTION FROM THE DEPARTMENT OF INORGANIC, PHYSICAL AND CATALYTIC CHEMISTRY OF THE INSTITUTE "NICOLAOS CANELLOPOULOS"]

## On Selective Catalysis

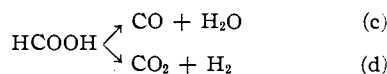
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### Introduction

One of the best means of investigating the factors determining the fitness of a certain catalyst for a given gas reaction, is the observation of relative selectivity in simultaneous reactions of one reactant. The best known example is the concurrence of dehydration and dehydrogenation, *e. g.*, in the reactions



or



It is well known that metals and zinc oxide catalyze predominantly the dehydrogenations (b) and (d), whereas other oxides, *e. g.*, alumina, are predominantly dehydration catalysts, accelerating (a) and (c). Sabatier,<sup>1</sup> on the ground of his purely chemical theory of intermediate compounds, considered selectivity as an intrinsic chemical property of the catalyst substance, and derived from his output measurements, series of chemical substances, extending from pure dehydrogenators through catalysts of a relative selectivity to pure dehydrators. But soon it was recognized that besides the chemical nature of the catalyst, its mode of preparation influences the direction of its action. Thus, Adkins,<sup>2</sup> by studying oxides originating from different compounds, came to the opinion that materials with large pores tend to split off hydrogen, and those with fine pores, water vapor. His findings have been interpreted differently by Taylor,<sup>3</sup> and Adkins himself later modified his views by the consideration of additional factors.

The application of modern catalytic kinetics to the problem involves the determination of the frequency factors and activation energies of both reactions on one catalyst, and their comparison. In this way, Hinshelwood<sup>4</sup> showed that in the case of formic acid on glass, the difference of the activation energies is much greater than would be expected from the ratio of the two velocities. This made it probable that the two reactions take place on different parts of the active surface independently. Rideal and Hoover,<sup>5</sup> working with ethanol on a partly selective thoria catalyst, showed that the dehydrogenation has the smaller activation

energy, and that it is selectively poisoned by water and chloroform and selectively reduced by increasing the pressure. They thus established the view of separate partial surfaces for each reaction.

Nevertheless, it remained astonishing that in so numerous cases, in spite of great differences of the activation energies, the ratio of the two velocities is not far from unity, *i. e.*, that the factor  $\exp(\Delta q/RT)$ , resulting from that difference and amounting to several orders of magnitude, is so often compensated by the ratio of the partial surfaces for each reaction. This difficulty is greatly reduced by the newer finding, obtained in this and many other laboratories, that the frequency factor is by no means a universal constant, as assumed by Hinshelwood, but is in turn a function of the activation energy. Let the velocity of dehydrogenation be

$$k_h = k_{oh}e^{-q_h/RT} \quad (1)$$

and of the dehydration

$$k_w = k_{ow}e^{-q_w/RT} \quad (2)$$

then, the selectivity is measured by

$$k_w/k_h = k_{ow}/k_{oh} e^{-(q_w - q_h)/RT} \quad (3)$$

Now, it has been shown<sup>6</sup> that

$$k_{oh} = ae^{q_h/h} \quad (4)$$

and

$$k_{ow} = ae^{q_w/h} \quad (5)$$

$a$  and  $h$  being constants,  $h$  sometimes depending on the preparation temperature of the catalyst, but not being greatly variable. Thus, we obtain

$$k_w/k_h = e^{(q_w - q_h)/h} \times e^{-(q_w - q_h)/RT} \quad (6)$$

At the temperature  $T = h/R$ , the selectivity becomes unity, in spite of the difference in the activation energy, and at the (usually not very distant) temperature of actual observation, it will, consequently, not be so far away from unity, as would be expected on ground of a universal value of  $k_0$ .

Of course, equations (4) and (5) are rough approximations, but, from this point of view, the coexistence of relative selectivity and of widely different activation energies is understandable without the assumption of widely different specific surface areas. This involves the possibility that the variations in selectivity actually observed with different catalysts, are not so much a matter of the activation energy, *i. e.*, of the chemical character of the catalyst, as supposed by Sabatier, as they are a matter of secondary variations of the other constants involved,  $h$  and  $a$ . Especially  $a$  in equations (4) and (5) need not be a constant but contains the extent of the partial surface area active for each of the reactions.

(1) P. Sabatier, "Catalysis in Organic Chemistry," Leipzig, 1927.

(2) H. Adkins, THIS JOURNAL, **44**, 2175 ff. (1922).

(3) H. S. Taylor, "Coll. Sympos. Monogr.," **4**, 19 (1926).

(4) C. N. Hinshelwood, H. Hartley and B. Topley, Proc. Roy. Soc. (London), **A100**, 575 (1922).

(5) G. I. Hoover and E. K. Rideal, THIS JOURNAL, **49**, 104, 116 (1927).

(6) G.-M. Schwab and N. Theophilides, J. Phys. Chem., **50**, 427 (1946).

In our laboratory during recent years methods have been worked out for a quick and reliable measurement of  $k_0$  and  $q$  of decomposition reactions of vapors,<sup>6</sup> and therefore we resolved to examine once more the questions of relative selectivity of dehydrogenation and dehydration, based on broad experimental data and having in mind the above newer theoretical viewpoints.

## Experimental

### A. Decomposition of Ethanol

**Materials.**—Kahlbaum absolute alcohol was the reactant. For the catalysts, outlines of the preparation are given first, followed by crystal analysis from X-ray examination.

**Zinc Oxide.**—I: Heating of zinc nitrate to 400°, formation of pellets (1 mm.) and reheating gave large isodiametric crystals. II: (See Hüttig<sup>7</sup>) zinc oxalate was precipitated from zinc chloride and ammonium oxalate, washed one hundred times, compressed to pellets and decomposed at 400°, giving small disturbed needles parallel to the  $c$ -axis. III: Zinc hydroxide was precipitated from zinc sulfate by adding ammonia, boiling, washing the product nineteen times and decomposing the pellets at 420° to disturbed plates perpendicular to the  $c$ -axis. IVb: This sample was prepared similarly to III, but starting with zinc chloride and decomposing the hydroxide at 260° to large isodiametric crystals. IVc: This was prepared like IVb but decomposing at 480° to give crystals like IVb. V: Zinc carbonate was decomposed at 360° to produce disturbed needles parallel to the  $c$  axis, somewhat larger than II. Zinc oxide reversed: was precipitated by hydrochloric acid from  $Zn(NH_3)_6Cl_2$  as very flat disturbed plates perpendicular to the  $c$ -axis.  $ZnCO_3$ : The starting material of V was decomposed during the ethanol catalysis; ZnO crystals like V.

**Titanium Dioxide, 300°:** Kahlbaum titanium hydroxide on heating to 300° gave an amorphous product. Anatase: the 300°  $TiO_2$  on heating to 600° gave anatase (octahedrite). Rutile was made by heating one of the previous compounds to 1000°.

**Chromic Oxide, 20°:** This was prepared by cold precipitation from nitrate with ammonia, losing water without the glowing phenomena, and dehydrating under catalytic conditions; the crystallographic investigation of chromium compounds is impracticable with the available  $FeK\alpha$  radiation. Glowed oxide was made by precipitation with ammonia in boiling sulfate solutions and glows spontaneously on dehydration. The (Hg) catalyst was made by heating mercuric chromate to about 700°.

**Aluminum Oxide,  $Al_2O_3$  ( $\gamma$ ),** was made by precipitating with ammonia from a chloride solution, and dehydrating at 300°; it is glassy with small crystallites of cubic  $\gamma-Al_2O_3$ . I( $\alpha$ ) comes from heating the former oxide to 1100° and is large crystals of corundum. II( $\alpha$ ) was made by heating aluminum oxide to 1400°, giving corundum crystals larger than I.

**Calcium Fluoride, Cold:** was made by precipitation from calcium chloride with hydrofluoric acid at room temperature as small fluorite crystals. Hot: was formed by precipitation from boiling solution. Kahlbaum commercial product was large fluorite crystals. 900°: Cold-precipitate calcium fluoride after heating to 900° was catalytically inactive.

**Tricalcium Phosphate, Cold:** was prepared by precipitation with ammonia and diammonium phosphate from excess calcium chloride at room temperature (Berzelius, 1845) in amorphous condition. 1000°: Heating the preceding material to 1000° produced amorphous solid.

**Ceric Oxide, 300°:** The Kahlbaum product was heated to 300° to form large crystals and amorphous material. 1050°: the previous material was heated to 1050°.

**Thorium Dioxide, 300°:** An amorphous form was made by precipitation with ammonia from partly basic chloride and heating to 300°. 600°: was made by heating the former to 300°, as small crystals. 1000°: large crystals were produced by heating the 300° material to 1000°. K1150°: the Kahlbaum preparation was heated to 1150°.

**C. Act.**—"Carbotox" charcoal from the Lurgi Company was in the form of very small graphite crystals. Graph. nat. was natural graphite scales, medium crystallites. Graph. synth. was large crystals of artificial graphite.

**Sodium chloride** was fused and broken up material.

**Barium sulfate** was made by cold precipitation.

**Sodium carbonate** was the commercial pellets.

**Sodium sulfate** was in the form of commercial pellets.

**Potassium iodide** was as crystal pieces.

**Ferrous sulfide** was fused and broken pyrrhotine.

**Apparatus.**—The left part A of Fig. 1 represents the apparatus already described<sup>6</sup> for the continuous observation of the change of reaction velocity with temperature, as improved by Schwab and Pesmatjoglou.<sup>8</sup> It is based on the reflux distillation of the liquid reactant so that its vapors pass over the catalyst at a variable and measured temperature. B is a wash bottle, through which the gaseous products are passed. The addition to be made for the present investigation is that two reaction velocities instead of one must be measured simultaneously so that a simple flowmeter is no more sufficient. In the case of the ethanol decomposition (reactions (a) and (b)), a mixture of variable amounts of hydrogen and ethylene leaves

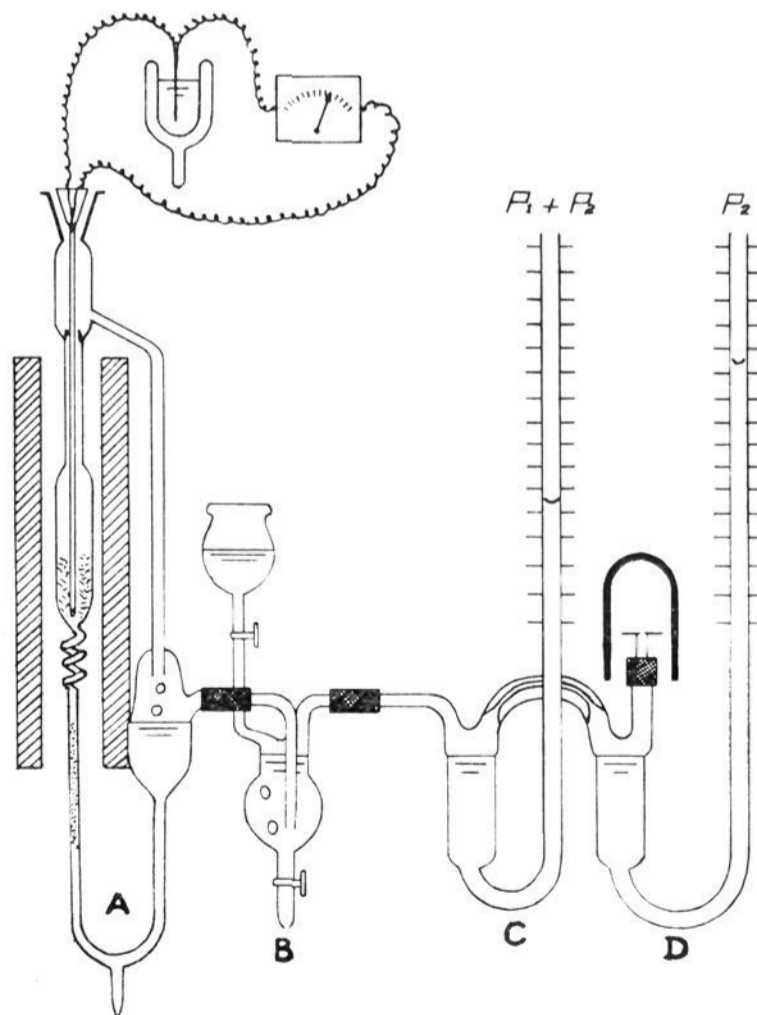


Fig. 1.

(8) G.-M. Schwab and S. Pesmatjoglou, *J. Phys. Coll. Chem.*, **52**, 1046 (1948).

(7) G. F. Hüttig, *Kolloidch. Beihefte*, **39**, 281 (1934).

B, and its flow rate and composition must be measured continuously and simultaneously. This is achieved by the simple arrangement C-D, applicable for numerous similar problems: C is a common capillary flowmeter of a sensitivity of 0.289 cc. of air/cm. water, being of a special device avoiding dead space. D is a similar instrument, but, instead of the capillary, its exit is a fine hole of about 0.03 mm. diameter in a thin gold foil, sealed to the exit tube and protected by an open glass bell. C measures the flow rate with a sensitivity proportional to the *viscosity* of the actual gas mixture, and D with a sensitivity proportional to its *density* (Bunsen principle). As viscosity and density of hydrogen-ethylene mixtures do not run parallel, the ratio C/D depends on the gas composition. In Fig. 2 a calibration diagram is given, obtained by the use of artificial mixtures. The indications of C are plotted against those of D for different compositions. Intermediate compositions are easily interpolated. (The deviation from linearity is due to the finite thickness of the foil.) The composition being thus known, the indication of C can be evaluated in absolute units on the basis of literature viscosity data.

### Procedure

In a sample of a few hundred milligrams of the catalyst the approximate pellet size distribution was determined microscopically and the geometrical surface estimated on the assumption of a cubic pellet shape. The mean pellet size was some tenths of a millimeter. Then the catalyst was mounted in the reaction chamber, the reactant poured into the storage bulb, and runs at rising and falling temperature carried out until both velocity and composition curves coincided in repeated runs. Between two runs, sometimes, the calibration of Fig. 2 was checked because it proved sensitive to contaminations of the hole.

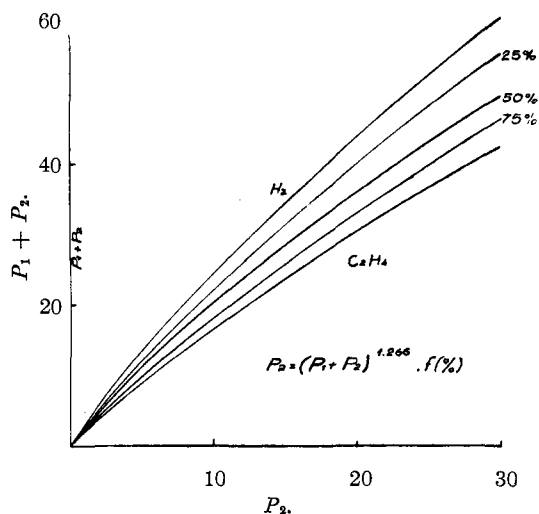


Fig. 2.

### Results

Different sets of runs were performed with most catalysts, often with different samples, and in each set the observations were continued until reproducibility was obtained.<sup>6</sup> In Table I, mean values of the results are given, obtained from a great number of runs. The first column indicates the catalyst, according to p. 1807, the second column, its geometrical surface area, determined as described. The third column gives an over-all activation energy  $q$  mixed of the over-all reaction, as taken from the temperature dependence of the first flowmeter readings C (these numbers are given because they are free of the relative uncertainty due to errors in the gas composition, especially at large excesses of either hydrogen or ethylene). The fourth column gives an idea of the actual interval of selectivity of the catalyst at the observation temperatures. Always the higher ethylene content refers to the upper temperature limit. The fifth and sixth columns contain the apparent activation energies of the separate reactions. The seventh and eighth columns indicate the temperature at which the hydrogen and ethylene evolution with the amount of catalyst actually present reaches a certain arbitrary amount, corresponding to a 10 cm. water column in the flowmeter C for air, or 2.89 cc./min. These numbers give an indication of the temperatures used. The ninth and tenth column give  $B$ , the logarithm to base ten of the temperature independent factor  $k_{oh}$  and  $k_{ow}$  of equation (1) and (2) for 1 sq. cm. of geometrical surface.

The position of the velocity-temperature curves, reduced to 1 sq. cm., is characterized within the limits of experimental accuracy by the numbers  $B$  and  $q$ . But it must be observed that in our case of two simultaneous reactions this is not as good a proof of the accuracy of these numbers themselves, as it is in single reactions. The splitting of  $q_{mixed}$  into  $q_{H_2}$  and  $q_{C_2H_4}$  and the calculation of  $B_{H_2}$  and  $B_{C_2H_4}$  from these are subject to the whole measure of uncertainty in the gas composition. This holds (see Fig. 2) especially in the case of very small ethylene contents ( $ZnO, TiO_2, Cr_2O_3$ ), where the abnormally large values of  $q_{C_2H_4}$  are probably considerably in error due to the probable presence of viscous by-products formed from acetaldehyde. Naturally,  $B_{C_2H_4}$ , as calculated from the observed  $10^3/T(v = 10)$  by the extrapolation to  $1/T = 0$ , is still more affected by this source of error, whereas the two reaction velocities themselves are approximately correct within the actual interval of observation. For this reason, the discussion will not so much be based on the  $B$  and  $q$  values but rather on the velocities themselves. For this purpose, the velocities, reduced to 1 sq. cm. of geometrical surface, are plotted logarithmically in Fig. 3 as function of  $1/T$ , separately for each catalyzing compound. In these diagrams, the horizontal  $10^3/T$  axis is drawn at an ordinate value corresponding to a velocity of 0.5 cc./min. or 0.2 cc./

TABLE I  
 RESULTS ON THE ETHANOL DECOMPOSITION

Catalyst	Geom. surf. sq. cm.	$q$ , mixed kcal.	$C_2H_4$ , %	$q_{H_2}$ kcal.	$q_{C_2H_4}$ kcal.	$10^3/T$ ( $v = 10$ ) $H_2$	$10^3/T$ ( $v = 10$ ) $C_2H_4$	$B_{H_2}$	$B_{C_2H_4}$
ZnO II	24	30	8-19	25	46	1.627	1.527	7.5	14.4
ZnO V	16	30	4-16	23	56	1.568	1.489	7.4	17.7
"ZnCO <sub>3</sub> "	36	32	5-14	25	56	1.560	1.478	7.4	17.2
ZnO I	24	25	2-14	18	48	1.453	1.326	4.8	13.1
ZnO III	13.5	25	9-20	20	39	1.544	1.431	6.1	10.7
ZnO IVb	18	21	5-14	17	43	1.520	1.383	4.5	12.3
ZnO IVc	20	24	2-16	20	46	1.469	1.391	5.8	13.2
ZnO reversed	42	28	27-35	25	37	1.560	1.528	7.5	11.2
	67	30	13-28	24	46	1.590	1.503	7.0	13.9
TiO <sub>2</sub> 300°	60	33	69-72	32	34	1.306	1.374	8.0	9.1
Anatase	50	31	15-25	25	51	1.408	1.327	6.6	13.6
Rutile	(~20)	31	8-30	24	59	1.307	1.293	(~7.4)	(~14.8)
Cr <sub>2</sub> O <sub>3</sub> 20°	21.3	22	57	22	22	1.432	1.462	6.2	6.4
Cr <sub>2</sub> O <sub>3</sub> glowed	15	39	7-26	28	68	1.461	1.406	8.3	20.2
Cr <sub>2</sub> O <sub>3</sub> (Hg)	13	25	7-25	20	48	1.420	1.334	5.6	13.6
$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	25	31	100	..	31	..	1.635	..	10.3
$\alpha$ -Al <sub>2</sub> O <sub>3</sub> I	9	28.5	78	28.5	28.5	1.290	1.378	7.5	8.1
$\alpha$ -Al <sub>2</sub> O <sub>3</sub> II	22	35	34-42	30	41.5	1.337	1.325	8.0	11.1
CaF <sub>2</sub> cold	42	40	100	..	40	..	1.480	..	11.9
CaF <sub>2</sub> hot	24	26	0-9	<26	>26	1.390	1.240	<7.1	>6.2
CaF <sub>2</sub> Kahlb.	44	29.5	20-40	22.5	45	1.266	1.234	5.2	11.1
Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> cold	40	35	100	..	35	..	1.490	..	10.4
Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> 1000°	46	33	25-40	27.5	43.5	1.283	1.255	6.55	10.3
CeO <sub>3</sub> 300°	24	30	18-25	26	38	1.540	1.475	7.6	11.5
CeO <sub>2</sub> 1050°	21	36	15-23	32	49	1.313	1.260	8.5	12.7
ThO <sub>2</sub> 300°	34	33	95	34	34	1.433	1.547	9.7	10.4
ThO <sub>2</sub> 600°	15	29	78-82	25	33	1.383	1.502	6.5	10.0
ThO <sub>2</sub> 1000°	16	36	45-50	32	41	1.215	1.216	7.6	10.3
ThO <sub>2</sub> K1150	33	28	65	28	28	1.414	1.457	7.7	7.9
C act.	(~20)	33	23-39	28	48	1.372	1.346	(7.3)	(13.4)
C graph. nat.	28	(33)	65	(28)	(48)	1.336	1.336	(6.6)	(11.3)
						( $v = 2.4$ )	( $v = 3.5$ )		
C graph. synt.	54	(33)	21	(28)	(48)	1.325	1.325	(6.0)	(10.0)
						( $v = 1.3$ )	( $v = 0.4$ )		
NaCl	30	31	0	31	..	1.320	..	8.0	..
BaSO <sub>4</sub>	27	29	0	27	..	1.372	..	7.9	..
Na <sub>2</sub> CO <sub>3</sub>	33		25-50			1.328	1.328		
						( $v = 3.5$ )	( $v = 1.9$ )		
Na <sub>2</sub> SO <sub>4</sub>			0			1.336			
						( $v = 12$ )			
KI			0			1.332			
						( $v = 0.5$ )			
FeS	30							0	0

min., and, for the sake of clearness, the ethylene (dehydration) curves are drawn in the upper half of every diagram only, and the hydrogen (dehydrogenation) curves in the lower half only. It will be seen below that this manner of representation leads to consistent results more directly than the  $B$  and  $q$  values.

(In two cases, some arbitrary assumptions had to be made in the construction of the diagrams: For titania, rutile and for active carbon the geometrical surface, not measured, was assumed to amount to the standard value of 20 sq. cm. and

for the two graphite specimens the activation energies of active carbon were used for the construction of the slope of the curves. The points of interest in our discussion will scarcely be affected by these arbitrary choices.)

### B. Decomposition of Formic Acid

**Materials.**—98% formic acid redistilled over anhydrous cupric sulfate was the reactant. Besides the catalysts already described, some others were used:

**Chromic Oxide, 500°.**—The 20° chromic oxide was heated at 500° for twenty-four hours.

**Chromic Oxide, Alkaline.**—Chromic chloride was converted to sodium chromite with sodium hydroxide, neu-

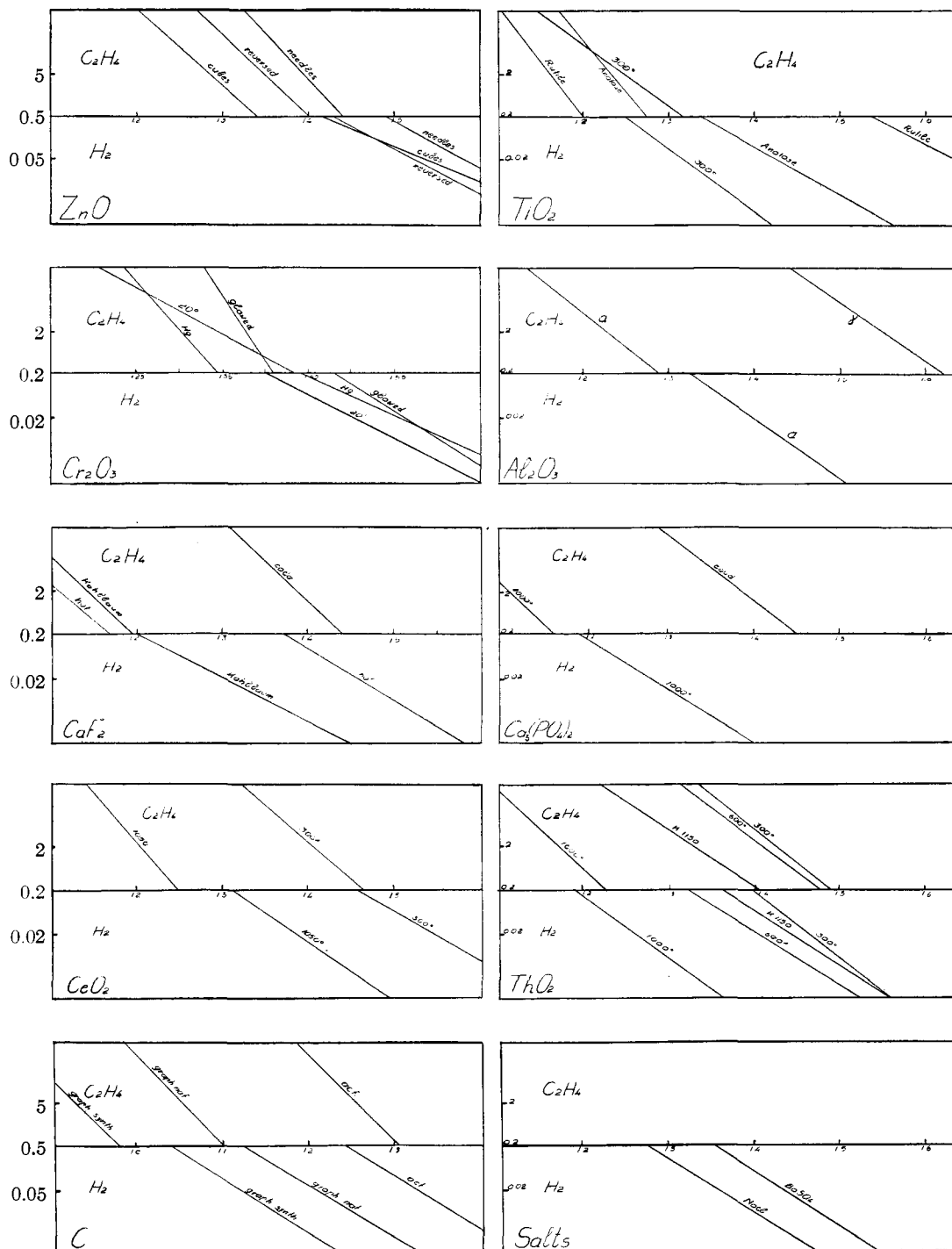


Fig. 3.

tralized with hydrochloric acid (green), precipitated at 100° with sodium carbonate, dried at 110°, pelleted and dehydrated in the catalysis atmosphere (not glowing).

**Aluminum Oxide, 970°.**— $\gamma$ -Alumina was heated to 970°, X-rays showing it to be  $\gamma$ - $Al_2O_3$ .

**$\alpha$ -Aluminum Oxide, 1100°.**—This was like  $\alpha$ - $Al_2O_3$  I.

**Aluminum Oxide, Inversed.**—Aluminum was dissolved in sodium hydroxide, partly precipitated at 100° with hydrochloric acid, dried at 110° and dehydrated in the

catalysis atmosphere, to the salt- or marble-like form as shown by X-rays to be  $\gamma$ - $Al_2O_3$ , very small crystallites, perhaps somewhat larger than those of  $\gamma$ - $Al_2O_3$ .

**Calcium Fluoride (Na).**—This form was precipitated from calcium chloride with sodium fluoride, and was very slimy in appearance.

**Silica, Cold.**—This was precipitated from dilute sodium silicate with hydrochloric acid, washed with acetone and dried at 110°.

TABLE II  
RESULTS ON THE FORMIC ACID DECOMPOSITION

Catalyst	Geom. surf. sq. cm.	CO, %	qH <sub>2</sub> kcal.	qCO kcal.	10 <sup>3</sup> /T (v = 10) H <sub>2</sub>	10 <sup>3</sup> /T (v = 10) CO	B <sub>H<sub>2</sub></sub>	B <sub>CO</sub>
ZnO III	24	8-4	30	23.5	1.73	(1.56)	11.0	7.65
Cr <sub>2</sub> O <sub>3</sub> 20°	12	68-57	34	27	1.658	1.730	12.3	10.1
Cr <sub>2</sub> O <sub>3</sub> 500°	9	16-10	37.6	30	1.657	1.574	13.7	10.4
Cr <sub>2</sub> O <sub>3</sub> alkal.	29	17-21	34	38!	1.684	1.647	12.1	13.2
γ-Al <sub>2</sub> O <sub>3</sub>	28	83-67	34	24	1.622	1.723	11.6	8.6
Al <sub>2</sub> O <sub>3</sub> 970°	30	100-95	(45)	27	1.63 (v = 1)	1.695	(14.5)	9.5
α-Al <sub>2</sub> O <sub>3</sub> 1100°	27.5	30-16	36	24	1.505	1.457	11.4	7.2
Al <sub>2</sub> O <sub>3</sub> inversed before C <sub>2</sub> H <sub>5</sub> OH	18	70-36	41	25.5	1.585	1.597	14.0	8.7
Same after C <sub>2</sub> H <sub>5</sub> OH	18	51-32	35	24	1.575	1.650	11.8	8.4
CaF <sub>2</sub> (Na)	18	7-3	39	21	1.763	1.570	14.8	6.0
CaF <sub>2</sub> cold II	36	3-0	37	24	1.62	1.62 (v = 0.62)	12.6	6.8
CaF <sub>2</sub> cold II	36	3-0	34	21	1.59	1.62 (v = 0.267)	11.3	5.3
C active	20	60-28	35.5	19.2	1.718	1.700	13.1	6.9
SiO <sub>2</sub> cold	30	100-95	35	23	1.676 (v = 1)	1.780	11.4	8.5
SiO <sub>2</sub> 1100°	36	4.5-2.5	30	22	1.550	1.506 (v = 1)	9.6	5.7

Silica, 1100°.—This form was made by heating the previous kind for two hours at 1100°.

Apparatus and Procedure.—The same arrangement and method was followed as de-

scribed for the ethanol work. In the formic acid decomposition, a continuous analysis of the hydrogen-carbon monoxide-carbon dioxide mix-

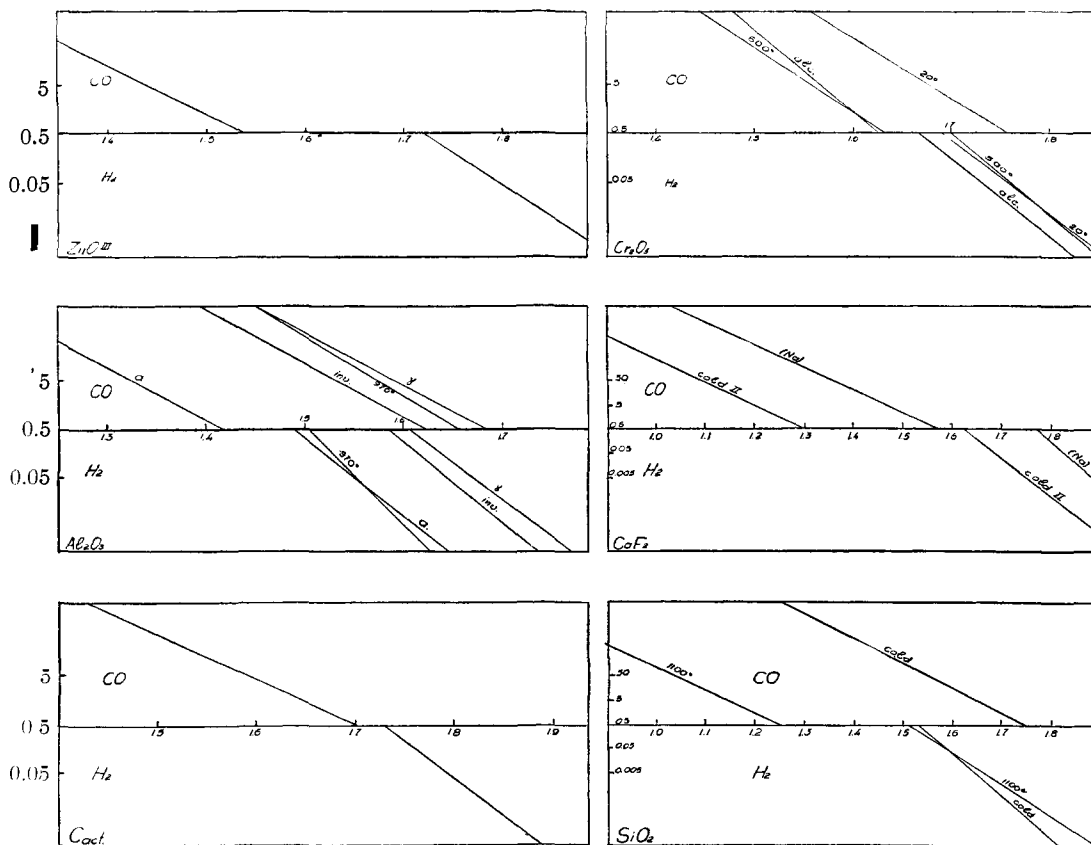


Fig. 4.

scribed for the ethanol work. In the formic acid decomposition, a continuous analysis of the hydrogen-carbon monoxide-carbon dioxide mix-

flowmeters (sensitivities 1.17 and 2.575 cc. of air per cm. of water).

(9) G.-M. Schwab and E. Schwab-Agallidis, *Ber.*, **76**, 1228 (1943).

TABLE III  
COMPARISON OF ETHANOL AND FORMIC ACID DECOMPOSITIONS

Catalyst	Formic acid reaction							Ethanol reaction						Mode of comparison	
	CO, %	$q_{H_2}$	$q_{CO}$	$\frac{10^3/T}{H_2} = 0.5$	$\frac{10^3/T}{CO} = 0.5$	$B_{H_2}$	$B_{CO}$	% $C_2H_4$	$q_{H_2}$	$q_{C_2H_4}$	$\frac{10^3/T}{H_2} = 0.5$	$\frac{10^3/T}{C_2H_4} = 0.5$	$B_{H_2}$		$B_{C_2H_4}$
ZnO III	8-4	30	23.5	1.72	1.545	11.0	7.65	9-20	19	42	1.418	1.338	5.6	12.0	Indirect
Cr <sub>2</sub> O <sub>3</sub> 20°	68-57	34	27	1.692	1.759	12.3	10.1	57	22.5	22.5	1.319	1.380	6.2	6.4	Indirect
Cr <sub>2</sub> O <sub>3</sub> alcal.	17-21	34	38!	1.665	1.624	12.1	13.2	18-24	44	56	1.173	1.355	11.0	16.3	Direct, before
$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	83-67	34	24	1.600	1.691	11.6	8.6	10-19	46	56	1.163	1.321	11.4	15.9	Direct, after
								100	..	31	..	1.533	..	10.3	Indirect
								100	..	34	..	1.470	..	10.64	Direct
$\alpha$ -Al <sub>2</sub> O <sub>3</sub>	30-16	36	24	1.486	1.426	11.4	7.2	~40	29	36	1.260	1.232	7.7	9.4	Indirect
Al <sub>2</sub> O <sub>3</sub> in-versed	70-26	41	25.5	1.590	1.605	14.0	8.7	35-50	42	42	1.274	1.274	11.4	11.4	Direct, before
	51-32	35	24	1.584	1.763	11.8	8.4	65	(42)	(42)	1.221	1.283	(11.2)	(11.5)	Direct, after
CaF <sub>2</sub> (Na)	7-3	39	21	1.770	1.586	14.8	7.0	0	(40)	..	(1.268)	..	(10.8)	..	Direct
C active	60-28	35.5	19.2	1.725	1.712	13.1	6.9	23-39	28	48	1.240	1.304	7.3	13.4	Indirect

### Results

The results are tabulated in Table II in the manner indicated for Table I (with the difference that  $10^3/T(v = 10)$  in columns 7 and 8 refers to a velocity of 10 cc./min.). The term  $q_{mixed}$  is not given, because here the separate  $q$ 's are of considerable accuracy and reproducibility.

In Fig. 4, the results are represented in the manner of Fig. 3, the  $1/T$ -axis having been drawn at an ordinate of 0.5 cc./min./sq. cm. and carbon monoxide being plotted above, hydrogen below this line. But it may be mentioned that in the case of formic acid because of the absence of side reactions, the values of  $B$  and  $q$  are of a considerably greater accuracy than those for ethanol.

### C. Comparison of Both Reactions

Some of the catalysts have been examined comparatively with formic acid and with ethanol. These comparisons are contained in Table III. In the cases marked "direct" the same specimen has been measured in both reactions, in the "indirect" comparisons different specimens of identical samples were used. No essential difference is observed. The words "before" and "after" indicate that the respective measurement was performed before or after a measurement with the alternative reactant. So, only a slight deactivation for the ethanol reaction by the formic acid treatment is observed for chromium oxide and aluminum oxide. In general, it is seen that the formic acid reaction proceeds at temperatures about 150° lower, but that nevertheless the selectivity (% carbon monoxide and % ethylene) in the temperature interval of comparable reaction velocities, is about the same for both reactions on all the catalysts. This phenomenon will be discussed below.

### Discussion of Results

**A. Activation Energies.**—The values of the activation energies of Table I, as already stated, are of moderate accuracy, especially  $q_{C_2H_4}$  in cases of low ethylene contents. Nevertheless, a critical review of these values reveals some regularities: In 24 out of 27 fully analyzed cases it is found that

$$q_{C_2H_4} > q_{H_2}$$

with a mean difference of  $\Delta q = 21 \pm 8$  kcal./mole. In five other cases this difference could not be measured because only one product was formed. This general behavior is in accordance with Rideal and Hoover's findings for thorium oxide and, thus, seems to be a property of the competing reactions themselves, nearly independent of the special catalyst. Table II reveals a similar fact in a more precise manner for the formic acid reactions. Here, conversely (with one doubtful exception, chromic oxide alkaline)

$$q_{H_2} > q_{CO}$$

(with a mean difference of  $\Delta q = 12 \pm 4$  kcal./mole). The meaning of these facts is that, in the case of ethanol, an increase of temperature favors the dehydration, whereas, in the case of formic acid, it favors the dehydrogenation.

Any distinct relation between the activation energy and the chemical nature or the physical state of the catalyst is not detectable; in the case of ethanol the values of  $q_{mixed}$  as well as the separate values  $q_{H_2}$  and  $q_{C_2H_4}$  are quite irregularly distributed; in the case of formic acid, they are much less scattered,  $q_{H_2}$  being always near 35 kcal./mole and  $q_{CO}$  near 24 kcal./mole, but, again, no systematic influence of the catalyst substance is observed. The only distinct finding of this kind is the following:  $q_{mixed}$  (which is more accurate and therefore more suitable for comparison) of the ethanol decomposition shows values of  $31 \pm 1$  kcal./mole on all those zinc oxide preparations which, by X-rays, are characterized as needle-shaped, and of  $23.5 \pm 1.5$  kcal./mole for isodiametric crystals. This seems to indicate a slightly different action of basal planes and of pyramidal or prism planes.

Likewise, no direct relation can be discovered between the activation energy and the selectivity ratio. It is not a general rule that the reaction with the lower activation energy is favored; if it were, only hydrogen would be produced from ethanol and only carbon monoxide would be produced from formic acid. Many examples have been found in which different catalysts show different activation energies for each of both reactions, but the selectivity is almost the same. This is the

TABLE IV  
 INTERRELATION OF THE ARRHENIUS CONSTANTS

Reactant	Reaction	$B_0$	$h$	$\theta$		$1/\theta \times 10^3$	$10^3/T_{\text{obs.av.}}$
				(°K.)	(°C.)		
$C_2H_5OH$	Dehydrogenation	-1.0	3650	799	526	1.250	1.29
$C_2H_5OH$	Dehydration	+0.3	3550	778	505	1.285	
HCOOH	Dehydrogenation	-2.5	2300	503	230	1.988	1.60
HCOOH	Dehydration	-2.4	2300	503	230	1.988	

case with ethanol in the previously mentioned two groups of zinc oxides or with different chromic and cerium oxides. *Vice versa* in many cases the selectivity varies largely at remarkably constant activation energies. Such cases are ethanol on zinc oxide reversed and zinc oxide needles, and nearly all the formic acid reactions.

These facts confirm our introductory hypothesis that the actual selectivity is not determined by the activation energy difference of the two reactions but rather by the ratio of the frequency factors  $h_0$  or the difference of their logarithms  $B$ .

### B. Frequency Factors

However, a discussion of this influence cannot be made simply by a comparison of the  $B$ -values of Tables I, II and III, because usually two catalysts or two preparations of one catalyst do not differ only in their  $B$ -values but also in their  $q$ -values. Now,  $B$ , as stated above, is a function of  $q$ , and, hence, the connection of selectivity with these magnitudes is rather complicated. Only the fact that we can base our considerations on a large number of catalysts and two different reactions, enables a rational discussion to be made with the statistical elimination of fortuitous single effects.

First of all, the function  $B(q)$  must be known. Inspection of Tables I, II and III shows at once that  $B$  rises with  $q$  as was supposed in equations (4) and (5). We found these equations, in their logarithmic form

$$B = B_0 + q/h = B_0 + q/R\theta \quad (7)$$

to hold very well for each of our four reactions. The constants  $B_0$  and  $h$  or  $\theta$ , calculated from the data of Tables I, II and III, are given in Table IV. It is seen, that, with formic acid as well as with ethanol, the two reactions give one common line,  $h$  being the same for dehydration and dehydrogenation. For ethanol, the  $\theta$ -value of this line coincides approximately with the average observation temperature  $T_{\text{obs.av.}}$ . This simply means that all the observed reactions reach the velocity 0.5 near that temperature, and that the experimental fluctuations of  $q$ , by way of the calculation, produce corresponding fluctuations of  $B$ . As for the real distribution function of the active centers, which again is of the type (4), (5), (7) (see Schwab, Taylor, Spence<sup>10</sup>), we only can say that its  $h$  or  $\theta$ -value is not far enough from the observed to produce a measurable deviation. For formic acid,  $\theta$  is considerably less than  $T_{\text{obs.av.}}$ , indicating that  $B$

depends on  $q$  much more than the mere existence of an average velocity would explain. In other words, in this case, large activation energies are over compensated by large  $B$ -values. (However, the meaning of a preparation temperature can scarcely be attributed to these  $\theta$ -values. This is quite natural as catalysts of very different nature and modes of preparation are compared.)

The significance of  $\theta$  for the present selectivity problem is as follows: As already pointed out, at this temperature both reactions are of equal velocity, provided that the two  $B$ - $q$  points lie on a line of the slope  $1/R\theta$  (line AB in the scheme of Fig. 5), and a shift in selectivity at the temperature  $\theta$  means a deviation from this line. *E. g.*, the cata-

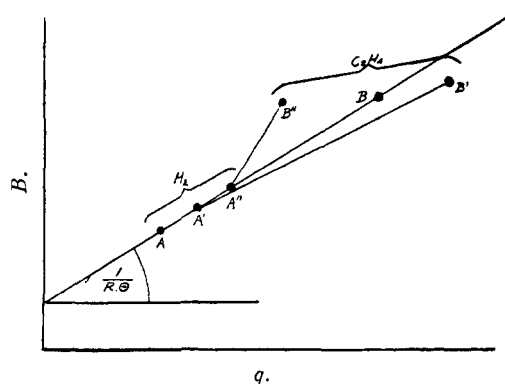


Fig. 5.

lyst characterized by the points  $A'$  and  $B'$  for the two reactions, respectively, will show the selectivity 1:1 at a higher temperature, and at the temperature  $\theta$  it will produce an excess of hydrogen, in spite of its higher  $B_{C_2H_4}$ . The transition from  $AB$  to  $A'B'$  may be due to a change of catalyst material, or equally well to a thermal treatment. Similarly, a catalyst  $A''B''$  will produce excess ethylene, in spite of its lower  $B_{C_2H_4}$ . We see that a change in selectivity does not simply mean a shift of  $B$ , but of the position of  $B$  in relation to the actual  $q$ -value.

From this point of view, one fact, shown in Table III and mentioned above, is of special interest. The selectivity of a catalyst for the formation of ethylene from ethanol is about the same as its selectivity for the formation of carbon monoxide from formic acid, and the change of selectivity by different modes of preparation is the same for both reactants. This appears striking in view of the fact that the reaction temperatures differ by about  $150^\circ$  and that the series of the two activa-

(10) G.-M. Schwab, H. S. Taylor and R. Spence, "Catalysis from the Standpoint of Chemical Kinetics," New York, N. Y., 1937.



tion energies is inverse for both reactants. At present, we understand that this fact simply means that in both cases a catalyst of, say, low dehydrating power has an abnormally low  $B$ -value for dehydration (*e. g.*,  $B'$  in Fig. 5) and *vice versa*. This reveals the important result, that *the active centers for the dehydration of ethanol and formic acid are identical*, and the same is true for the centers of *dehydrogenation*.

For the absolute value of  $B$  Schwab and Theophilides<sup>6</sup> give a theoretical upper limit of 10.7 for 15 sq. cm. or 9.6 for 1 sq. cm. In a series of papers (see recent ones<sup>11,12</sup>) it has been shown that this value on smooth metallic surfaces can be exceeded by one unit, on rough broken surfaces by even more. Thus, it is not surprising that the porous oxide catalysts used here show  $B$ -terms up to 14 at the highest  $q$ -values. (The highest values of the order of 18 are probably not real owing to the already repeatedly mentioned overestimation of the temperature coefficient of low ethylene contents.)

### C. The Selectivity

According to the preceding paragraph, the special influences of the catalyst's nature and treatment on  $B$  can be discussed only if the simultaneous unsystematic variations of  $q$  are taken into account. Obviously this sort of discussion would be very complicated. It has been shown that the direct consideration of the selectivity (gas composition) itself contains *in nuce* these combined influences and is much more simple. Therefore, the influences of preparation will be discussed with the aid of Figs. 3 and 4, which contain the measured partial velocities.

**Zinc Oxide.**—This catalyst is rather insensitive to different modes of preparation. The needle-shaped and the isodimensional crystals both show predominant dehydrogenation of ethanol and of formic acid, the former preparations giving slightly greater velocities for both the ethanol reactions. The only way to favor slightly the dehydration is the inverse precipitation which raises the ethylene content from 5–15% to 15–35%. As these crystals are plate-shaped, it is possible, in accordance with other results mentioned below, that the flat interstices between the plates are the preferential seat of the dehydration.

**Titanium Oxide.**—The thermal treatment increases considerably the dehydrogenation reaction and leaves nearly unaltered the dehydration, thus raising the hydrogen content of the products. As in the course of this treatment a considerable intragranular shrinking is observed, changing the compact pellets to spongy aggregations, it is more logical to assume that the dehydrogenation remained about unchanged and the dehydration decreased, referred to the actual internal surface.

(11) See ref. 8.

(12) G.-M. Schwab and A. Karatzas, *J. Phys. Coll. Chem.*, **52**, 1053 (1948).

**Chromic Oxide.**—In the case of ethanol, it is seen that three preparations of very different origin show very different activity (and activation energy) for the ethylene formation, but all nearly the same hydrogen formation. Still more significant is the behavior in the formic acid reaction. Heating to 500° leaves the hydrogen evolution quite unaltered whereas the dehydration is heavily reduced. The special preparation "chromic oxide alkaline" is similar to the 20° preparation with an unspecifically reduced total surface.

**Calcium Fluoride.**—This is an example showing that the general aspect of the phenomena is not restricted to oxides. Fluorite, precipitated at 20° in small crystals, forms only ethylene from ethanol. Heating during precipitation shifts the dehydration to so much higher temperatures (*cf.* aluminum oxide) that the hydrogen evolution becomes observable. The Kahlbaum preparation seems to be an intermediate, but of smaller total surface. Formic acid is dehydrated by the two sorts of fluorite used there, and they differ in carbon monoxide production more than in hydrogen production.

**Aluminum Oxide.**—From ethanol,  $\gamma$ -alumina forms practically only ethylene, as has been known for a long time. Here, it is most interesting that heating to 1100° changes this absolutely selective catalyst into one of relative selectivity, mainly by an enormous reduction of the dehydrating surface. The course of this change may be followed in the formic acid reaction because, here, the  $\gamma$ -oxide gives some hydrogen. Heating to 970° has a very slight effect on the dehydration and a greater one on the dehydrogenation. On further heating to 1100° this latter remains in its final state, whereas only now the enormous reduction of dehydration, mentioned above, occurs. Inversed precipitation is another way of preparing a dehydrogenating alumina, as again ethylene is more affected by the change of structure than is hydrogen.

**Calcium phosphate** behaves exactly like calcium fluoride or alumina, heat lowering mainly or even exclusively the dehydration.

**Ceric oxide** gives a heat deterioration, larger for ethylene than for hydrogen.

**Thorium Oxide.**—Heating to 600° affects the dehydration slightly and the dehydrogenation more strongly; but, on further heating, as in the case of aluminum oxide, the reduction of the dehydration surpasses that of the dehydrogenation, so that again the 1000° preparation is a good dehydrogenator. The heated Kahlbaum preparation is in the same state, but has a larger total surface.

**Carbon.**—The crystal size increases in the series: active carbon, carbon, graphite natural, carbon, graphite synthetic. In the same series both reaction velocities decrease, the dehydration more than the dehydrogenation. On active carbon, formic acid behaves about like ethanol.

**Silicon Dioxide.**—Heating very clearly affects the dehydration of formic acid strongly and the dehydrogenation not at all.

**Other Catalysts.**—Compact, crystallized salts, as sodium chloride, potassium iodide, barium sulfate and sodium sulfate, have no dehydrating and weak dehydrogenating properties. Only sodium carbonate, which probably is a porous desiccation product, catalyzes both reactions. Ferrous sulfide has no action at all on ethanol.

### Conclusions

In all the examples studied the selectivity is not an intrinsic property of the catalyst substance. Very generally, on oxides as well as on salts and carbon, and with two different reactants, factors increasing crystal size and surface shrinking decrease the partial surface active in dehydration by a higher degree than they do the surface of dehydrogenation. Such factors are: the precipitation at elevated temperature, heating of the sample, transition from active charcoal to natural and synthetic graphite. Opposite factors are certain modes of preparation. It is possible, by heating, to change a typical dehydrating catalyst, as aluminum oxide, thorium oxide, calcium phosphate, silicon dioxide, into a partially dehydrogenating one, and, *vice versa*, by reversed precipitation, in order to prepare the usually dehydrogenating zinc oxide in a partially dehydrating form. In many cases, the dehydrogenations are entirely invariant to the mode of preparation.

The most probable explanation of these facts is the assumption, somewhat similar to that of Adkins, that the dehydrogenations take place mainly on the flat surface of the catalyst particles (crystallites or aggregations of such—"secondary particles" according to Fricke<sup>13</sup>) and that the dehydration is restricted to submicroscopical holes, cracks, pores or channels between those particles. It is easily imagined that on recrystallization these pores will disappear to a much higher degree than the flat surface decreases. Especially the narrow circular crevasses around the contact points of two particles will first be filled and flattened out on recrystallization.

We tried to get an idea about the dimensions of the dehydrating cracks by electron microscopy. Our  $\gamma$ -aluminum oxide, giving 100% ethylene from ethanol and 83–67% carbon monoxide from formic acid, is of glass-like appearance like silica gel, and our "aluminum oxide inversed," giving only about 50% carbon monoxide from formic acid, is of a salt- or marble-like appearance. Under the microscope the  $\gamma$ -pellets appear compact, the "inversed" pellets white and porous. Obviously this porosity has no relation to the dehydration pores, which must be more frequent in the  $\gamma$ -oxide. Prof. Feitknecht and Dr. Studer had the kindness to take photographs 1:7000 of the two

(powdered) preparations in the electron microscope of the University of Berne (Switzerland). They are reproduced in the Figs. 6 and 7. Even under this enlargement the  $\gamma$ -aluminum oxide still appears compact. This indicates that the dehydrating pores, if they exist, are smaller than about 100 Å.



Fig. 6.

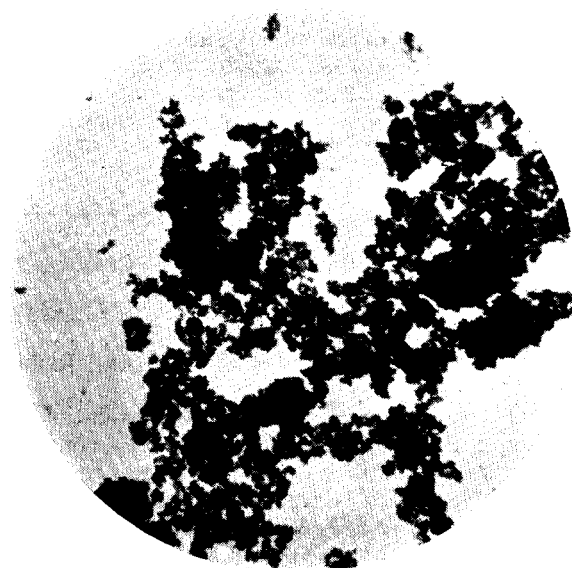
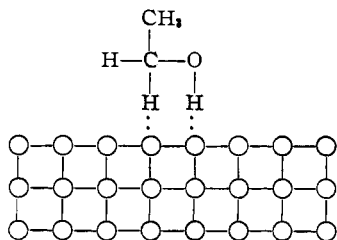


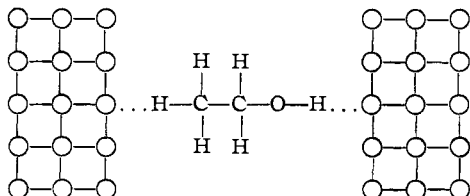
Fig. 7.

Thus, they probably are of molecular dimensions. This would imply a modification of Balandin's well-known doublet hypothesis, in the sense that the doublet acting in dehydrogenation consists of two neighboring catalyst atoms acting on hydrogen atoms.

(13) R. Fricke in G.-M. Schwab's "Handbuch der Katalyse," Vol. 4, Vienna, 1943, p. 1.



whereas in the dehydration an attack on the substrate molecule is necessary *from two opposite sides, i. e.*, from the two walls of a molecular crack.



The fact that, at least in the alcohol dehydration, the hydrogen atom and the hydroxyl group are most probably split off from different carbon atoms, is in favor of this view. Even in the opposite case of formic acid a similar mechanism seems probable by analogy to solution catalysis. Acid-base catalyzed hydrolysis, which is about the reverse of dehydration, is well known<sup>14</sup> to be a prototropic change, requesting an electron shift by the simultaneous action of a proton donor from one end and a proton acceptor from the other end of the reactant molecule. In the extreme form of dual ionization catalysis, this view of the prototropic character of the heterogeneous dehydration has recently been expressed by Bremner.<sup>15</sup> Experiments to check this view are planned.

(14) R. Bell, J. Baker, *et al.*, in G.-M. Schwab "Handbuch der Katalyse," Vol. 2, Vienna, 1941.

(15) J. G. M. Bremner, *Research*, 1, 281 (1948).

## Summary

The velocity of the simultaneous dehydration and dehydrogenation of the vapors of ethanol and of formic acid on many different oxides and salts as catalysts has been examined. Activation energies and frequency factors were measured by a reflux flowing system with the use of special methods of continuous product gas analysis.

With ethanol, the dehydration has the greater activation energy, whereas with formic acid the dehydrogenation activation energy is greater. A systematic dependence of the activation energy on the chemical nature and the mode of preparation of the catalysts does not exist.

A linear relationship between the activation energy and the logarithm of the frequency factor has been shown to exist, identical for both reactions, but different for the two reactants.

After taking into account the casual variations of the activation energies, it is shown that the different degree of selectivity is mainly due to differences of the frequency factors.

For these reasons, the actual ratio of reaction velocities at a reference temperature gives an adequate picture of the variations of the two selectively active surface areas.

The results indicate that factors producing sintering or recrystallization most generally reduce the rate of dehydration to a larger degree than that of dehydrogenation, independently of the chemical nature of the catalyst.

It is concluded that probably dehydrogenation takes place on the flat surface of the secondary particles, and dehydration within cracks of molecular dimensions. Arguments in favor of this view are discussed.

ATHENS (PIRAEUS), GREECE RECEIVED OCTOBER 25, 1948

• [CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KANSAS]

## Further Studies on the Oxidation of Sodium in Liquid Ammonia

BY WILLIAM H. SCHECHTER,<sup>1</sup> JOSEPH K. THOMPSON AND JACOB KLEINBERG

The data in the literature on the oxidation of sodium in liquid ammonia have been of a conflicting nature. Joannis<sup>2</sup> stated that a substance of the formula  $\text{Na}_2\text{O}\cdot\text{NH}_3$  is first formed and this is further oxidized to  $\text{Na}_2\text{O}_3$  when a solution of sodium in liquid ammonia at  $-50^\circ$  is oxidized by a slow stream of oxygen. The investigations of Kraus and Whyte<sup>3</sup> on the slow oxidation of sodium in liquid ammonia have shown that sodium monoxide ammonolyzes in liquid ammonia to give a mixture of hydroxide and amide. The analyses of Jo-

annis upon which the formation of  $\text{Na}_2\text{O}\cdot\text{NH}_3$  are based would also correspond to a mixture of hydroxide and amide and it is, therefore, highly likely that this mixture was the first product of oxidation. Joannis' claim for the existence of  $\text{Na}_2\text{O}_3$  is based solely on an analysis for sodium, the oxygen content being calculated by difference. The work of Kraus and Whyte<sup>3</sup> has demonstrated that the amide in the mixture of hydroxide and amide formed by the ammonolysis of sodium monoxide may be further oxidized to nitrite. Consideration of the stoichiometry of these reactions leads to fact that the sodium content of the final mixture ( $3\text{NaOH}$  to  $1\text{NaNO}_2$ ) is very nearly that which would be present in a substance of the

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(2) Joannis, *Compt. rend.*, 116, 1370 (1893).

(3) Kraus and Whyte, *This Journal*, 48, 1781 (1926).